AECL Research

CALORIMETRY FOR A Ni/K_2CO_3 CELL

by

M.T. Craw-Ivanco, R.P. Tremblay, H.A. Boniface and J. Hilborn

CALORIMETRY FOR A Ni/K$_2$CO$_3$ CELL

by

M.T. Craw-Ivanco, R.P. Tremblay, H.A. Boniface and J. Hilborn

SUMMARY

Experiments were conducted to assess the possibility of excess heat production in light-water electrolytic cells. The program comprised six basic experiments in which the magnitude of heat production was monitored calorimetrically over a period of several days. The first three experiments were conducted with a relatively high power (about 10 W). In the first two experiments, there was an indication that some significant recombination of the electrolysis gases was occurring; therefore, an experiment was conducted in which a hydrogen/oxygen recombiner catalyst was introduced to the electrolysis cell. No conclusive evidence of excess power generation was observed. These experiments were performed at power levels in excess of those recommended by Randell Mills, of Hydrocatalysis Power Corporation (HPC). The electrode assembly was modified by Randell Mills, and on the direction of HPC a second series of experiments was conducted at lower power (~1 W), this time with ambiguous results because of measurement difficulties. In the higher power experiments (#1, #2 and #3), no net excess or deficit energy was observed greater than experimental error. According to Mills, this result was consistent with operation at currents and voltages substantially higher than 1 mA·cm^{-2} and 2.5 V. The lower power experiments were done within the recommended current density and voltage, and according to Mills the expected excess heat would be about 0.25 W. Various methods of analysis were applied to the results of experiments #4, #5 and #6. Some of these analyses indicated possible excess heat at approximately this level. A model was developed to help elucidate the heat transfer characteristics of the system and hence give some insight to the energy balance data for low-power experiments.

1. INTRODUCTION

Since the original claims of excess heat production in electrolytic cells by Pons and Fleishman, a considerable body of work has emerged, both experimental and theoretical. Fairly comprehensive reviews of the literature have been given recently.[1,2] While the original "excess heat generation" experiments concentrated on heavy-water solutions and noble metal cathodes, more recently several studies to investigate excess heat production with a K_2CO_3/light-water electrolyte in an electrolytic cell with a nickel cathode and platinum anode have been reported.[3-6]

The inventor of this work is Randell Mills, of Hydrocatalysis Power Corporation (HPC), who has reported excess power generation of 50 to 100% of the input electrical power with constant current and as high as 10 to 15 times input power with pulsed current.[6] Our work aimed to repeat the experiments of Randell Mills, to determine whether excess heat generation was observable in our experimental system. The experimental program was therefore conducted in close collaboration with personnel from HPC.

2. EXPERIMENTAL

2.1 Materials and Supplies

Potassium carbonate was purchased from the Aldrich Chemical Company and certified to be 99.99% pure. Nickel wire was obtained from Alfa Chemicals and all gases used came from Linde. Distilled 18 MΩ·cm deionized water was used for making up the electrolyte solution. To ensure no contamination of the electrode system all glassware was washed in HCl, rinsed copiously with distilled water and dried overnight in a vacuum oven at 200°C. In the first experiment, the cathode and anode were dipped in concentrated HCl for one hour, and then rinsed thoroughly with distilled de-ionized water. In subsequent experiments, the anode was treated as in experiment 1, but the cathode material was immersed in a 0.57 M K_2CO_3/3%H_2O_2 solution for thirty minutes, and then rinsed with distilled de-ionized water.[7] Once the cell had been cleaned all manipulations were carried out using nylon gloves. At no time were the electrodes immersed in electrolyte solution without current flowing. In experiment #3, AECL wetproofed catalyst # QA87-204 was inserted into the top of the electrolysis cell, to ensure complete recombination of all of the electrolysis gases.

2.2 Cell Design

To reproduce the conditions of Mills' experiments, a new cell was designed and constructed, as shown in Figure 1. The cell volume was approximately 1200 mL. The electrode support was constructed from polypropylene. The central cathode comprised 100 m of 0.5 mm nickel wire. Around the outer section of the electrode support, six 4-mm diameter glass rods were positioned (~1 cm from the central cathode) to support the 1.5-mm diameter platinum wire anode. The ratio of cathode to anode surface area was approximately 20:1. For the first experiment the electrode wires were connected directly to the power supply; for subsequent experiments the anode and cathode wires were clipped at the point of exit from the electrolyte solution and replaced by #16 American Wire Gauge (AWG) copper wire, to minimize resistive losses. The cell was stirred with a magnetically coupled glass stirring-rod assembly fitted with a Teflon paddle. Electrolysis gases were passed from the cell via the vent tube and a molecular sieve drier to a Tylan thermal mass flow transducer, to determine the quantity of gas being released from the cell. The mass flow transducer was calibrated using a stoichiometric (2:1) H_2/O_2 gas mixture against a soap bubble meter. Gases emitted from the electrolysis cell were sampled and analyzed by gas chromatography. The ratio of hydrogen to oxygen in the effluent from the cell was found to be 2.14:1.00.

1. INTRODUCTION

Since the original claims of excess heat production in electrolytic cells by Pons and Fleishman, a considerable body of work has emerged, both experimental and theoretical. Fairly comprehensive reviews of the literature have been given recently.[1,2] While the original "excess heat generation" experiments concentrated on heavy-water solutions and noble metal cathodes, more recently several studies to investigate excess heat production with a K_2CO_3/light-water electrolyte in an electrolytic cell with a nickel cathode and platinum anode have been reported.[3-6]

The inventor of this work is Randell Mills, of Hydrocatalysis Power Corporation (HPC), who has reported excess power generation of 50 to 100% of the input electrical power with constant current and as high as 10 to 15 times input power with pulsed current.[6] Our work aimed to repeat the experiments of Randell Mills, to determine whether excess heat generation was observable in our experimental system. The experimental program was therefore conducted in close collaboration with personnel from HPC.

2. EXPERIMENTAL

2.1 Materials and Supplies

Potassium carbonate was purchased from the Aldrich Chemical Company and certified to be 99.99% pure. Nickel wire was obtained from Alfa Chemicals and all gases used came from Linde. Distilled 18 MΩ-cm deionized water was used for making up the electrolyte solution. To ensure no contamination of the electrode system all glassware was washed in HCl, rinsed copiously with distilled water and dried overnight in a vacuum oven at 200°C. In the first experiment, the cathode and anode were dipped in concentrated HCl for one hour, and then rinsed thoroughly with distilled de-ionized water. In subsequent experiments, the anode was treated as in experiment 1, but the cathode material was immersed in a 0.57 M K_2CO_3/3%H_2O_2 solution for thirty minutes, and then rinsed with distilled de-ionized water.[7] Once the cell had been cleaned all manipulations were carried out using nylon gloves. At no time were the electrodes immersed in electrolyte solution without current flowing. In experiment #3, AECL wetproofed catalyst # QA87-204 was inserted into the top of the electrolysis cell, to ensure complete recombination of all of the electrolysis gases.

2.2 Cell Design

To reproduce the conditions of Mills' experiments, a new cell was designed and constructed, as shown in Figure 1. The cell volume was approximately 1200 mL. The electrode support was constructed from polypropylene. The central cathode comprised 100 m of 0.5 mm nickel wire. Around the outer section of the electrode support, six 4-mm diameter glass rods were positioned (~1 cm from the central cathode) to support the 1.5-mm diameter platinum wire anode. The ratio of cathode to anode surface area was approximately 20:1. For the first experiment the electrode wires were connected directly to the power supply; for subsequent experiments the anode and cathode wires were clipped at the point of exit from the electrolyte solution and replaced by #16 American Wire Gauge (AWG) copper wire, to minimize resistive losses. The cell was stirred with a magnetically coupled glass stirring-rod assembly fitted with a Teflon paddle. Electrolysis gases were passed from the cell via the vent tube and a molecular sieve drier to a Tylan thermal mass flow transducer, to determine the quantity of gas being released from the cell. The mass flow transducer was calibrated using a stoichiometric (2:1) H_2/O_2 gas mixture against a soap bubble meter. Gases emitted from the electrolysis cell were sampled and analyzed by gas chromatography. The ratio of hydrogen to oxygen in the effluent from the cell was found to be 2.14:1.00.
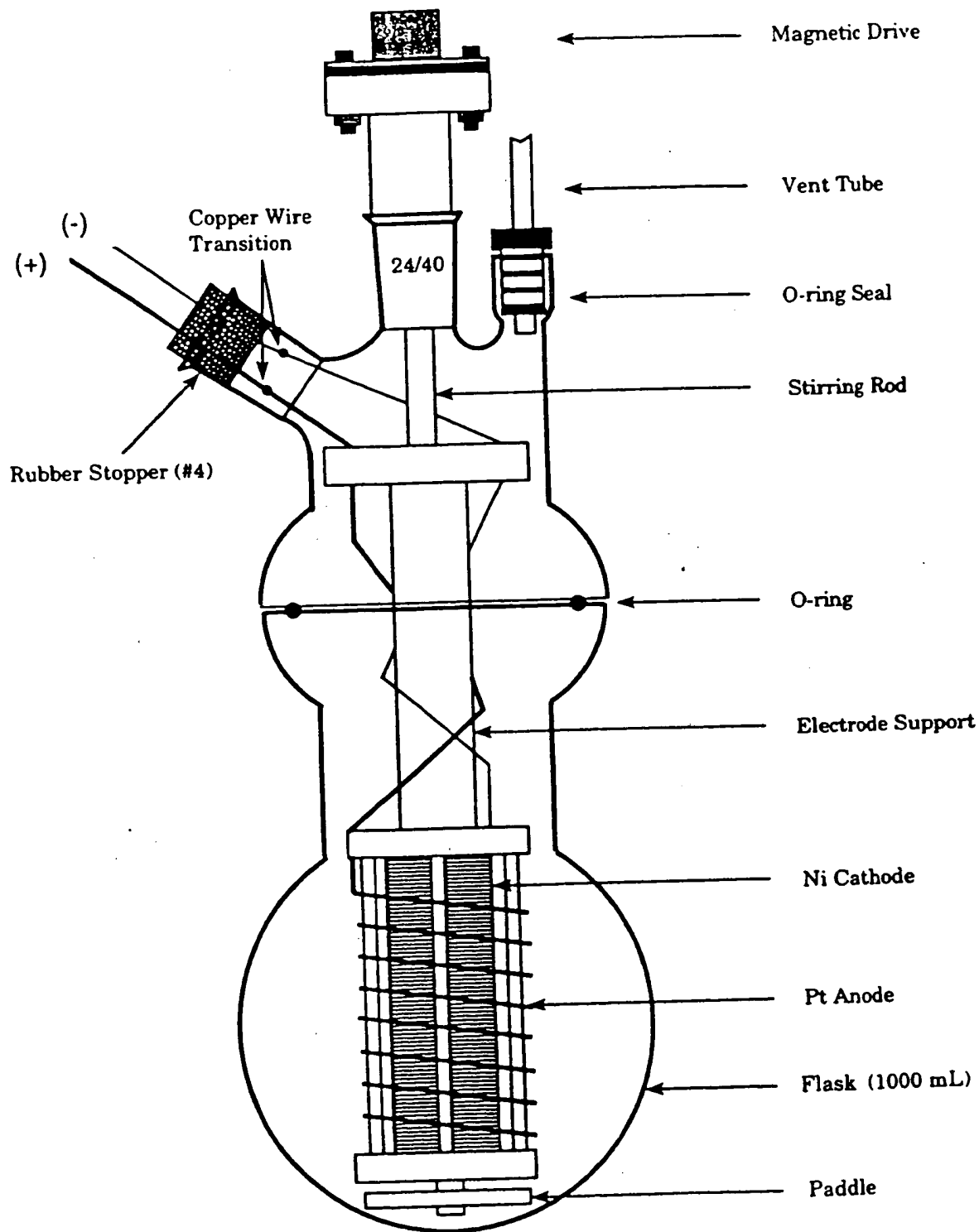
Magnetic Drive

Vent Tube

(-)

(+)

Copper Wire
Transition

24/40

O-ring Seal

Stirring Rod

Rubber Stopper (#4)

O-ring

Electrode Support

Ni Cathode

Pt Anode

Flask (1000 mL)

Paddle

Figure 1 - Electrolysis Cell

2.3 Temperature Control

A temperature-controlled enclosure was employed for these experiments, to ensure that fluctuations in the ambient temperature would not adversely affect the experimental results. The entire experimental system is shown in Figure 2, and a schematic illustrating the system water flow is shown in Figure 3. The ambient temperature in the enclosure was controlled by heat lamps, a cooling coil and a fan to circulate the air in the enclosure (minimum 2.5 $m^3 \cdot h^{-1}$).

2.4 Operating Conditions

The electrolysis cell was immersed in water inside the stainless-steel dewar and surrounded by a coil of copper tubing. Water was circulated through this coil to absorb heat from the cell when electrolysis was occurring. The experiment was designed in such a way that, for a given current, the theoretical heat generation was calculated and the inlet temperature of the water flowing through the copper coil adjusted such that the outlet temperature from the cooling coil would be approximately equivalent to the dewar temperature and the ambient temperature of the enclosure.

The ambient temperature and the dewar temperature were chosen as 35 to 37°C. The inlet temperature of water to the cooling coil was approximately 22 to 24°C, and the outlet temperature was approximately equal to the dewar temperature. The water circulating in the cooling coil was stored in a 25 L reservoir tank and passed through a constant temperature water bath (to obtain a temperature of 22 to 24°C) via insulated lines and a heat exchanger (to further ensure the appropriate inlet temperature) to the cooling coil in the dewar. The flow rate of water was controlled and monitored by an HPLC pump; as a check on the flow rate, the water was also passed to a weighing tank, which, when full, emptied into a drain tank equipped with a level controller and recycle loop to re-fill the water reservoir. In this way, the experiment could be run continuously with minimum operator intervention.

System temperatures, exit gas flow rate, water flow rate, voltage and current were all monitored and stored using a Data Translation DT2805 computer data acquisition system linked to a PC. A computer program was written for data acquisition and signals were recorded.

2.5 Instrumental Uncertainties and Estimation of Experimental Errors

Components of the experimental system were calibrated and where possible the experimental uncertainty associated with each of the following measurements was established or, where necessary, calculated:

i.   - Voltage, current and hence input power.
ii.   - Temperature measurements.
iii.   - Flow rate of water to cooling coil.
iv.   - Power from recombination of gases.
v.   - Resistive losses in lead wires.
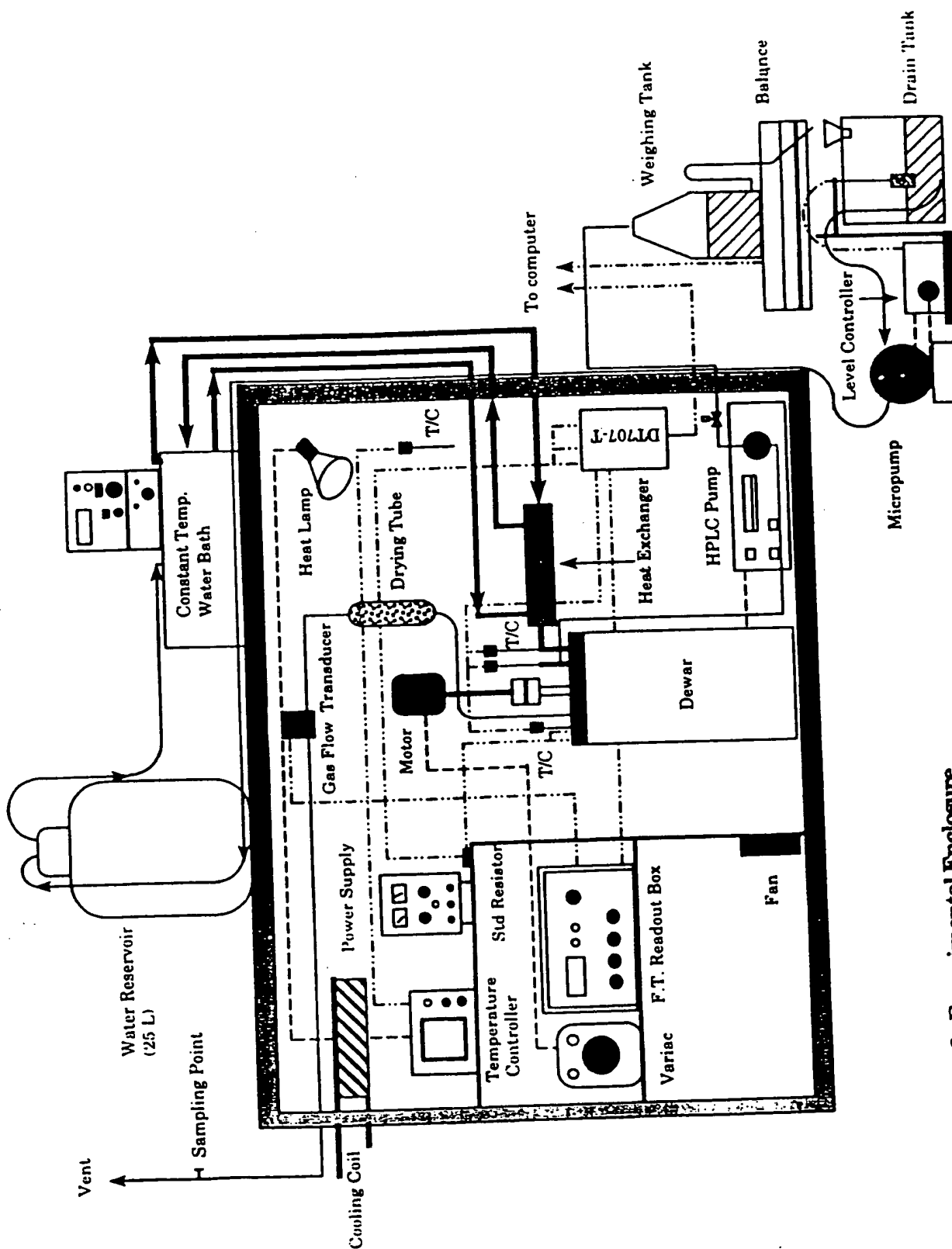vi.   - Effect of ambient temperature on dewar temperature.
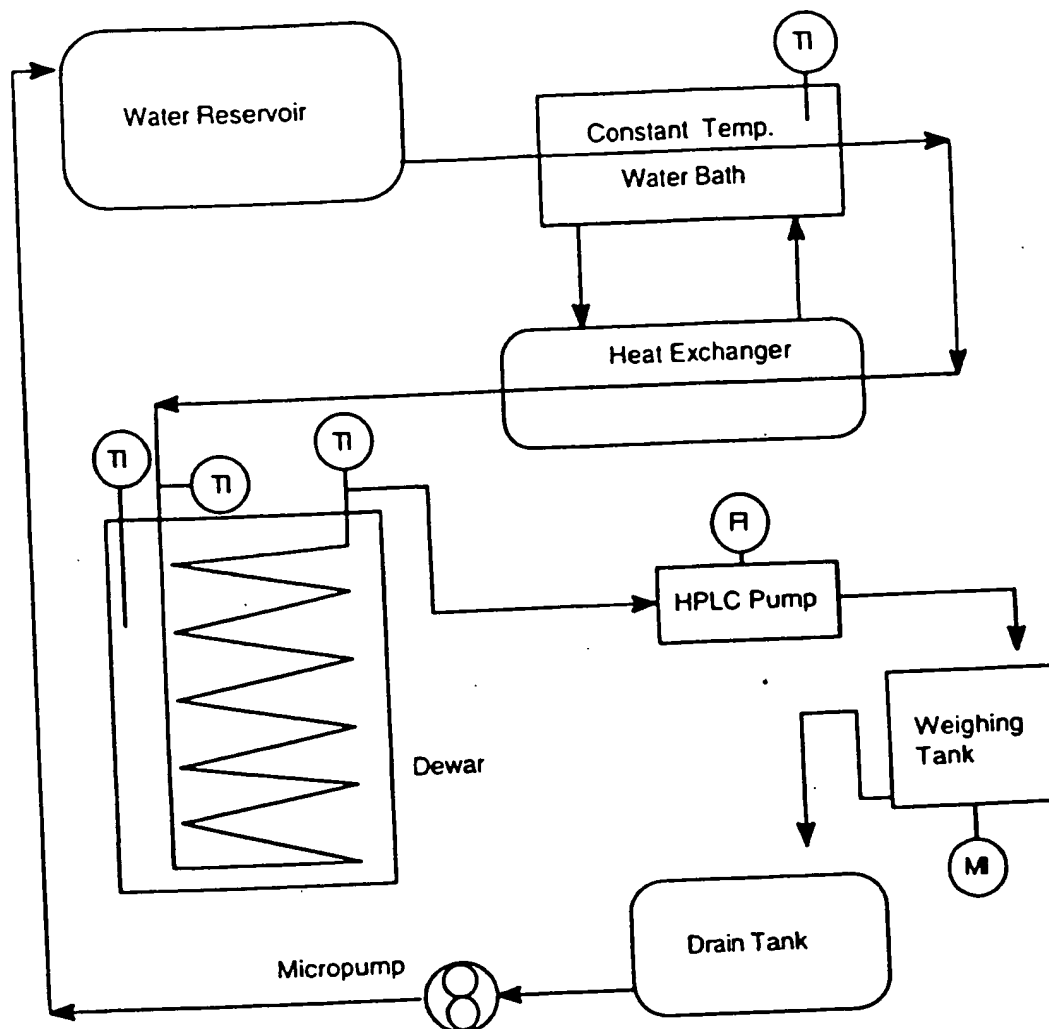
Figure 2 - Experimental Enclosure

Figure 3 - Water Flow Diagram

i. Voltage and Current Measurements

The voltage and current were recorded with the computer data acquisition system. The DT2805 board A/D subsystem has an accuracy of ± 0.1% FSR and a precision of ± 1 LSB (0.025%). The computer readout was compared with a 4.5 digit Fluke 8060A electronic multimeter. All readings were in agreement to four significant figures. The voltage was measured across supply wires near the entry to the cell, as shown in Figure 4. The current was obtained by measuring the voltage drop across a 10 W, 100±1 mΩ resistor. The exact resistor value was obtained using the voltage drop measured by the computer and the current flowing through the resistor as measured by a Fluke 8060A and a Fluke 77 multimeter. The resistor value was found to be 103.8 ± 2.3 mΩ over the operating range. The input power was calculated from:

$$Power = Voltage \times Current$$

The error associated with the calculation of the input power is estimated to be approximately ±2.2%.
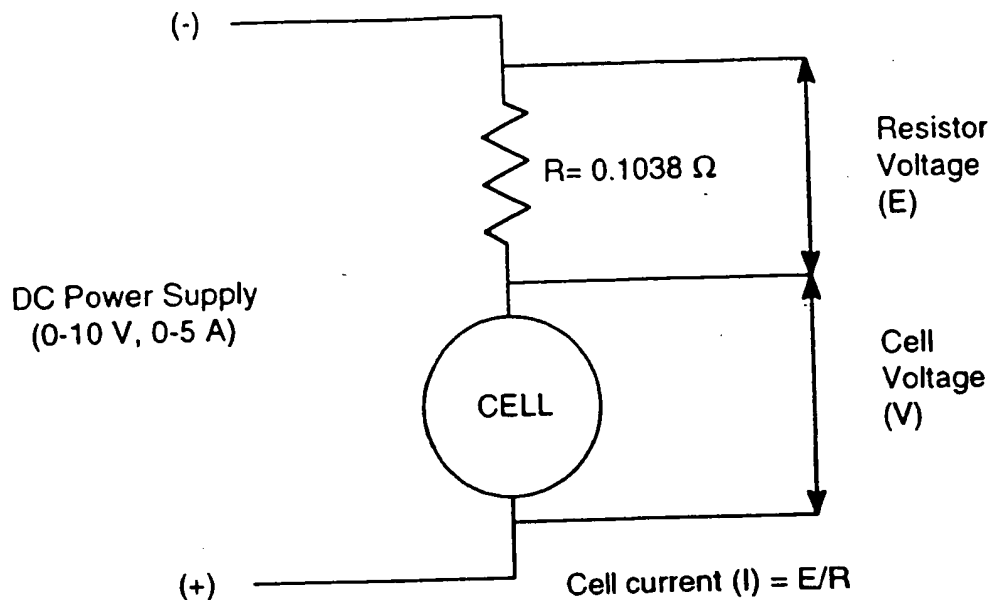
Figure 4 - Cell Electrical Measurements

ii.   Temperature Measurements

A Data Translation DT707-T screw terminal panel was used to make all the connections to the Data Translation DT2805 data acquisition board. The DT707-T is equipped with a thermocouple cold-junction compensation circuit (CJC). The CJC circuit provides a means by which to determine the temperature of the DT707-T board. The computer program was written to permit compensation for errors by the cold-junction thermocouple formed at the DT707-T. The CJC was calibrated following the procedure described in the user manual.

Since the board was located inside the test enclosure, the temperature of the board was used as a measure of the ambient temperature in the enclosure. The water inlet, outlet, and dewar temperature were measured using copper-constantan thermocouples (Type T, Limits of error ± 1°C). The temperature difference between the water inlet and outlet was used in the calculation to determine the power output of the cell. Small variations in the temperature measured by two independent thermocouples can occur. To eliminate this type of potential repeatability error, the two thermocouples used to measure the water inlet and outlet temperature were matched so that both thermocouples indicated the same temperature when immersed in an ice bath or in boiling water to within 0.1°C.

The thermocouples were calibrated and the error associated with ΔT measurements at the input and output of the cell were found to be within ±0.35%.

iii.   Flow Rate of Cooling Water

The flow rate of cooling water was controlled with the HPLC pump. The water was passed through the cooling coil and then to a reservoir situated on top of a balance. The mass of water in the reservoir was monitored (using the computer), and after approximately 100 minutes the average flow rate was calculated and compared with the flow rate reading recorded with the pump. The pump value for cooling-water flow rate was determined to be accurate to ±0.3%. The output power from the cell was calculated using the mass reading from the balance. If the balance reading fell below 98% of the pump reading, then the pump average flow was used to calculate the output power.

The power derived from the electrolytic cell (P_{cool}) was calculated according to the following equation:

$$P_{cool} = QC_p\Delta T$$

where:

C_p is the heat capacity of liquid water and taken as 4.184 $J \cdot g^{-1} \cdot K^{-1}$,

ΔT is the difference in temperature between the inlet and outlet of the cooling coil, and

Q is the flow rate of water to the cooling coil in $g \cdot s^{-1}$ (as determined from the balance).

The limit of accuracy attainable for power out measurements is estimated to be within 2%.

iv.   Power from Recombination of Electrolytic Gases

Recombination of hydrogen and oxygen produced on electrolysis is possible, and therefore all gases being released from the cell must be measured and accounted for. The power associated with recombination may be calculated from:

$$P_{rec} = \Delta H_{300\ K} (Q_{calc} - Q_{meas}) \times \frac{2}{3} \times \frac{1}{22.4}$$

where:

P_{rec} = the power added to the system from recombination of hydrogen and oxygen,

$\Delta H_{300\ K}$ = - 285.771 $kJ \cdot mol^{-1}$,[8] enthalpy of formation of H_2O (g) from H_2 and O_2 in their standard states at 298 K and 101.325 kPa,

Q_{calc} = gas flow rate ($L \cdot s^{-1}$) from the cell assuming no recombination,

Q_{meas} = actual exit dry gas flow rate ($L \cdot s^{-1}$) as measured experimentally,
2/3 accounts for stoichiometric ratio of hydrogen and oxygen, and
22.4 L is the volume occupied by one mole of a gas at STP.

The instrumental error on the mass flow transducer used for gas flow measurements is estimated to be ± 1%.

v.   Estimation of Resistive Losses in Lead Wires to the Cell

Resistive losses in the lead wires to the cell were calculated based on the following data:

Platinum wire #16 AWG has a resistive loss of 0.000764 $\Omega \cdot cm^{-1}$ at 18°C.[9] The length of wire from the cell to the power supply was approximately 31 cm; therefore, total resistance was approximately 0.024 Ω. For nickel wire, #16 AWG, the resistance is given as 0.00381 $\Omega \cdot cm^{-1}$.[9] The length of nickel wire used was ~39 cm; therefore, the total resistance in the nickel wire is estimated to be 0.15 Ω. Power associated with these two resistances may be calculated from:

$$P_{res} = I^2 R$$

Which, for experiment #1, was:

$$P_{res} = I^2(R_{Pt}+R_{Ni})$$
$$= (2.822 \text{ A})^2 \times (0.024 \ \Omega+0.15 \ \Omega)$$
$$= 1.38 \text{ W}$$

To minimize these losses, the platinum and nickel lead wires were replaced with #16 AWG copper wire. The resistance of this wire is documented as 0.000132 $\Omega\cdot$cm^{-1}.[9] Using 39 cm of copper wire for each electrode with a current of 2.822 A, the total resistive losses drop to 0.082 W. Therefore, copper was substituted for the nickel and platinum lead wires after the first experiment. In experiments #4, #5, #6, and in the calibration runs Cal1W1 and Cal1W2, the current never exceeded 1 A; therefore, the resistive losses in the copper lead wire were always less than 5.15 x 10^{-3} W.

vi.   Estimation of Fluid Frictional Power in a Pipe

The power loss due to the friction of the cooling water flowing in the cooling tube (P_{fr}) may be estimated, assuming the flow is laminar. Using the Hagen-Poiseuille equation for frictional head loss (Δp) in a circular tube:

$$\Delta p = \frac{128 \ \mu LQ}{\pi D^4}$$

Assuming a 10 m long tube (L) with a 2 mm inside diameter (D) and about 10 g·min^{-1} pure water flowing inside (Q), the head loss is:

$$\Delta p = \frac{128 \times 10^{-3} \ \frac{kg}{m \cdot s} \times 10 \ m \times \frac{10^{-5} \ m^3}{60 \ s}}{\pi \times (0.002 \ m)^4}$$
$$= 424 \text{ Pa}$$

and the power is:

$$P_{fr} = Q\Delta p$$
$$= \frac{10^{-5} \ m^3}{60 \ s} \times 424 \text{ Pa}$$
$$= 7.1 \times 10^{-5} \text{ W}$$

Thus, for this situation, the frictional power is negligible.

vii.   Estimation of Stirring Power Loss

Power added to the system by stirring may be estimated from the following correlations for the dimensionless power number (N_p):[10]

$$N_p = \frac{80}{R_e} \text{ at low Reynolds number}$$
$$= 6 \text{ at high Reynolds number}$$

where:

$$N_p = \frac{P_{st}}{\rho N^3 D^5}$$

$$Re = \frac{D^2 N \rho}{\mu}$$

In this case, the impeller was 40 mm diameter (D) and rotating at 2 rev·s⁻¹ (N) in electrolyte ($\rho = 1000$ kg·m⁻³, $\mu = 10^{-3}$ kg·m⁻¹·s⁻¹). Thus the power added by stirring was between:

$$P_{st} = \frac{80\,\mu}{D^2 N \rho} \rho N^3 D^5$$
$$= 80\,\mu N^2 D^3$$
$$= 80 \times 10^{-3} \frac{kg}{m \cdot s} \times (2s^{-1})^2 \times (0.04\ m)^3$$
$$= 2 \times 10^{-5}\ W$$

and:

$$P_{st} = 6\,\rho\,N^3 D^5$$
$$= 6 \times 10^3 \frac{kg}{m^3} \times (2s^{-1})^3 \times (0.04\ m)^5$$
$$= 5 \times 10^{-3}\ W$$

Therefore, in the worst-case scenario the power added to the cell from stirring is about 5 mW.

2.6   Estimation of Total Power In and Total Power Out of Cell

The total power delivered to the cell has several potential sources and may be calculated from:

$$P_{tot,in} = P_{e,in} + P_{rec} + P_{fr} + P_{st}$$

where:

$P_{e,in}$ is power from voltage and current delivered to the cell,
P_{rec} is power from recombination of electrolysis gases,
P_{fr} is power from the frictional pressure drop in the cooling coil, and
P_{st} is power produced from the stirrer.

The total electrical power provided to the cells is simply:

$$P_{e,in} = IV$$

and the power used for the electrolysis reaction is:

$$P_{elec} = IV_0$$

where:

V = the total cell voltage,
V_0 = the hydrogen/oxygen thermoneutral cell voltage (1.48 V), and
I = the cell current in A.

P_{rec}, P_{fr} and P_{st} are calculated as shown in Section 2.5.

The total output power from the cell can also be estimated:

$$P_{tot,out} = P_{cool} + P_{elec} + P_{res} + P_{cond}$$

where:

P_{cool} is the portion of input power used to heat up the cooling water,

P_{elec} is the portion of input power used in electrolysis of water,

P_{res} is the resistive losses in the lead wires, and

P_{cond} is the portion of power used to evaporate the water that is carried out (as vapor) with the evolved gases.

In a similar fashion the total input energy and output energy can be defined as:

$$E_{tot,in} = E_{e,in} + E_{rec} + E_{fr} + E_{st}$$

and,

$$E_{tot,out} = E_{cool} + E_{elec} + E_{res} + E_{cond}$$

or:

$$E_{tot,in} = \int_{t_1}^{t_2} P_{e,in}\, dt + \int_{t_1}^{t_2} P_{rec}\, dt + \int_{t_1}^{t_2} P_{fr}\, dt + \int_{t_1}^{t_2} P_{st}\, dt$$

and,

$$E_{tot,out} = \int_{t_1}^{t_2} P_{cool}\, dt + \int_{t_1}^{t_2} P_{elec}\, dt + \int_{t_1}^{t_2} P_{res}\, dt + \int_{t_1}^{t_2} P_{cond}\, dt$$

2.7   System Calibration

The cell was calibrated using a $1\ \Omega$ resistor as an immersion heater. This resistor was installed on the electrode assembly and the cell filled with de-ionized distilled water. The resistor was connected to the power supply using 1 m of #16 AWG copper lead wires. The ambient temperature was set at $37°C$ and the inlet power set to the desired value. After all the temperatures and process conditions were stabilized, the water flow rate and inlet temperature were adjusted such that the power output matched the power input.

Once the power input and output were matched, the data acquisition system was reset and the system was monitored over an extended period of time, to determine whether there was any drift, offset or fluctuation in the input or output power of the system. The mean input and output power for 7 W and 15 W calibration studies, along with standard deviations of these measurements, are shown in Table 1.

Temperature measurements were recorded during the resistance heater power calibration studies, to determine whether small fluctuations in the ambient temperature had any effect on the dewar temperature or the recorded outlet temperature. There was no significant effect of variations in the ambient temperature on the dewar temperature, providing the fluctuations in the ambient temperature were kept to a minimum. Mean temperatures with standard deviation data are listed in Table 1. Similar experimental data are also listed in Table 1 for the pump calibration and the mass-flow transducer calibration.

Table 1 - Statistical Analysis of Calibration Data

Quantity	Mean	Standard Deviation	% Error
Input Power (7 W)	7.35	0.0123	0.17
Output Power (7 W)	7.49	0.1673	2.22
Input Power (15 W)	14.56	0.0391	0.26
Output Power (15 W)	14.76	0.2603	1.78
Pump Flow (0.12 g·s^{-1})	0.12	0.0004	0.28
Pump Flow (0.24 g·s^{-1})	0.24	0.0007	0.29
Vent Gas Flow Rate (mL·min^{-1})	26.53	0.14	0.52

3. RESULTS

Experiments #1, #2 and #3

In all of these experiments, 1200 mL of 0.57 M K_2CO_3 solution was placed in the electrolysis cell. The cell current was set at 0.25 A before the electrode assembly was immersed in the electrolyte, in accordance with the directions from Mills' Laboratory.[7] After inserting the electrode and sealing the cell, the current was increased to 2.822 A, to give a current density of 1.8 mA·cm^{-2}. The system was operated until the dewar temperature and outlet temperature from the copper coil surrounding the cell were stabilized.

The voltage corresponding to this cell current was 4.93 V, which resulted in an input power of 13.86 W being delivered to the cell. Of this 13.86 W, it is expected that 4.177 W would be used for electrolyzing water (assuming electrolysis voltage equals 1.48 V). The remainder of the power would be used to increase the temperature of the water circulating around the electrolysis cell in the copper coil. The basic energy balance data for experiments #1, 2 and 3 were computed as shown in Table 2.

The surface area of the cathode was about 1500 cm^2. The current density recommended by Mills was less than 1 mA·cm^{-2}, thus the recommended current was about 1.4 A. The actual current was approximately twice this value. Furthermore, Mills recommended that the cell voltage not exceed 2.5 V. Using the cell resistance calculated from the voltage and current of experiment #1, the recommended input parameters were a cell current of 1.4 A, a cell voltage of 2.1 V and an input power of 2.94 W .

Table 2 - Data from Experiments #1, #2 and #3

Expt. #	Electrical Energy In (W·h)	Thermal Energy Out (W·h)	Total Electrolysis Energy (W·h)	Measured Gas Released (L)	Theoretical Gas Production (L)
1	723.6	517.1	212.6	67.59	89.80
2	1154.5	685.3	481	184.25	203.15
3	1196.7	1203.97	-	-	-

The total input energy to the cell may be calculated as follows for experiment #1:

$$E_{tot,in} = E_{e,in} + E_{rec} + E_{fr} + E_{st}$$
$$= 723.6 \text{ W·h} + 52.4 \text{ W·h} + 0 \text{ W·h} + 0.26 \text{ W·h}$$
$$= 776.3 \text{ W·h}$$

$$E_{tot,out} = E_{cool} + E_{elec} + E_{res} + E_{cond}$$
$$= 517.1 \text{ W·h} + 212.6 \text{ W·h} + 70.25 \text{ W·h} + 2.91 \text{ W·h}$$
$$= 802.7 \text{ W·h}$$

The first experiment was designed to identify potential operating problems. Recombination appeared to play a significant role in the overall energy balance; therefore, it was concluded that the absolute quantity of gas evolved from the system should be monitored very closely, and that particular attention should be paid to all potential leaks. Another possible source of error was resistive losses in the lead wires.

The quantity of water evaporated from the cell and adsorbed in the trap for experiment #1 was calculated by weighing the molecular sieve trap before and after the experiment. The mass of liquid adsorbed on the molecular sieve was recorded as 4.3 grams or 0.24 moles of water (which corresponds to a saturation temperature of about 40°C in the gas leaving the cell). The enthalpy of vaporization is approximately 44 $kJ \cdot mol^{-1}$.

From the integrated data there would appear to be an overall energy gain of 26.4 W·h in experiment #1, which would translate to approximately 0.5 W of power, or 3% of the input power. It is believed that, under the conditions of the experiment, this figure is within experimental error. According to the experiments of Mills et al., excess power to the extent of 1 $mW \cdot cm^{-2}$ of cathode surface would be expected, which in this experiment would translate to 1.5 W of power or an energy of 76.4 W·h.

In experiment #2, the reaction system was modified slightly, to minimize all potential power losses, ensure that there were no gas leaks and ensure that the measurement of gas evolution was indeed accurate. Further advice was sought from Randell Mills, of HPC, concerning operating conditions.

Prior to beginning the second experiment, a new cathode was rolled as described in Experiment 1. The cathode was then soaked in K_2CO_3/3% H_2O_2 as described in section 2. The platinum wire was soaked in HCl, rinsed in distilled deionized water and installed in the electrode assembly. A 0.57 M solution (1200 mL) of K_2CO_3 was placed in the electrolysis cell, the current turned on at 0.25 A and the electrode assembly immersed in the electrolyte. Since the nickel and platinum lead wires were replaced with copper, the overall cell resistance was reduced; therefore, for a current of 2.822 A the voltage required dropped to approximately 3.5 V. Hence, the input power to the cell was in the region of 9.87 W.

The surface area of the cathode was about 1500 cm^2. The current density recommended by Mills was less than 1 $mA \cdot cm^{-2}$, thus the recommended current was about 1.4 A. The actual current was approximately twice this value. Furthermore, Mills recommended that the cell voltage not exceed 2.5 V. Using the cell resistance calculated from the voltage and current of experiment #1, the recommended input parameters were a cell current of 1.4 A, a cell voltage of 1.83 V and an input power of 2.57 W

Approximately 9% of the expected electrolysis gas was missing, implying that this portion of gas had recombined. The energy associated with this recombination is calculated as 44.5 W·h. In addition, a small fraction of water vapor was carried from the cell in the effluent gas stream and adsorbed in the molecular sieve trap. The quantity of water adsorbed in the trap was calculated by weighing the molecular sieve trap before and after the experiment. The mass of liquid adsorbed on the molecular sieve was recorded as 11.7 grams or 0.65 moles of water (which corresponds to a saturation temperature of about 40°C in the gas leaving the cell - as in experiment #1). The energy lost from the system as a result of evaporation was calculated as 28.6 kJ or 7.9 W·h.

Summing up all the appropriate input terms for experiment #2:

$$E_{tot,in} = E_{e,in} + E_{rec} + E_{fr} + E_{st}$$
$$= 1154.5 \; W \cdot h + 44.5 \; W \cdot h + 0 \; W \cdot h + 0.578 \; W \cdot h$$
$$= 1199.7 \; W \cdot h$$

Similarly, the total power released from the cell, neglecting heat loss, can be obtained:

$$E_{tot,out} = E_{cool} + E_{elec} + E_{res} + E_{cond}$$
$$= 685.3 \; W \cdot h + 481 \; W \cdot h + 9.4 \; W \cdot h + 7.9 \; W \cdot h$$
$$= 1183.6 \; W \cdot h$$

The energy difference is therefore 16 W·h (or 0.14 W), or 1.4%. This energy is, however, apparently lost from the system, and we suspect that this "loss" reflects the operating constraints of the system.

One of the areas of concern in this type of experiment is accounting for energy added to the system from recombination of the electrolysis gases. One way to eliminate any uncertainty concerning recombination would be to recombine all of the electrolysis gas in a closed reactor. In order to do this another experiment was conducted identical to Experiment #2, but with a recombiner catalyst housed in the top portion of the electrolysis cell. The electrolysis cell was run under a slight excess of oxygen (2 mL·min^{-1}) to eliminate potential explosion hazards.

The difference in input and output energy can be computed as before:

$$E_{tot,in} = E_{e,in} + E_{rec} + E_{fr} + E_{st}$$
$$= 1196.7 \ W·h + 0 \ W·h + 0 \ W·h + 0.561 \ W·h$$
$$= 1197.3 \ W·h$$

Similarly, the total energy released from the cell can be obtained:

$$E_{tot,out} = E_{cool} + E_{elec} + E_{res} + E_{cond}$$
$$= 1203.97 \ W·h + 0 \ W·h + 9.44 \ W·h + 0 \ W·h$$
$$= 1213.4 \ W·h$$

Net energy production during the recombination experiment was therefore 16.1 W·h, which translates to 0.13 W or 1.3% of input power. This quantity of energy falls within the experimental error expected for this experiment. There would therefore not appear to be any real evidence for excess heat production in the large-scale cell as constructed and operated in this laboratory.

On further consultation with Randell Mills, it was agreed that the cell assembly would be sent to HPC, where a new anode and cathode would be fitted, the cell returned to AECL and a fourth experiment conducted. HPC provided analysis of AECL's departures from their protocol concerning operating conditions necessary for the observation of excess heat in a light-water electrolytic cell:

1. The cathode should not be electrolyzed above 2.5 V nor 1 amp current.
2. Rigorous cleaning steps as described in Section 2 should be conducted.
3. Back pressure in the cell must be avoided at all costs: at a partial pressure of 0.1 atm hydrino molecules, the catalytic reaction reaches equilibrium. Further tests with open cells demonstrated the higher the back pressure on an open cell, the less excess heat was observed for that cell.

These points were noted and the experimental system modified accordingly.

Experiments #4, #5 and #6

The electrodes were assembled at HPC using the AECL electrode holder. The cathode was constructed from three 30.76 m lengths of 0.38 mm nickel (Alfa Chemicals); the 1.5 mm diameter platinum wire anode was that of experiments #1, #2 and #3. The surface area of the cathode was 1 101.4 cm^2. To ensure that the conditions of the experiment were adhered to, the cell voltage was set at 2.4 V. With this voltage the current never exceed 1 A. Assuming no excess power generation, the actual power expected was in the region of 1 W. In order to detect this relatively small amount of power, the cooling water flow rate was reduced significantly, to ensure that the temperature change of the cooling water was high enough to be recorded accurately.

According to HPC, this electrode system was expected to produce a maximum of 1 mW·cm^{-2} of the cathode which carried a current of approximately 1 mA·cm^{-2}. The cathode surface area was 1100 cm^2 and it was estimated that approximately half was exposed to the electrolyte. Thus, the predicted excess power was approximately 0.25 W which, with this experimental arrangement, would amount to 25% excess power.

Experiment #4 was an open cell, whereas in experiments #5 and #6, the cell used for experiment #4 was fitted with the same recombiner catalyst used in experiment #3. These two experiments were

then run in the same way as experiment #3, except that in experiment #6 the water cooling was turned off and the run was quite short.

Calibration Runs

At the end of experiment #6, the power was turned off, but the experiment was allowed to continue in order to study the transfer of heat between the dewar and the surroundings. Following this, two low-power calibration tests were performed with a 1 Ω resistor arranged in the same way as the previous calibrations. In addition, a number of different heat transfer tests were done on the dewar. (These calibration runs were clearly desirable for an experimental setup that was designed for power measurements in the 10 W range, but was now being used for experiments in the 1 W range.)

The following tables (Table 3a, 3b and 3c) lists the experimental sequence of events for the last two experiments and the two calibration runs. The data in Tables 3b and 3c were obtained by averaging 10 readings starting at the times indicated.

Table 3a - Procedure for Experiments #5 and #6 and Calibrations #1 and #2

Experiment number	Date started	Duration (h)	Experiment duration (min)	Procedure description
5a	July 26	42	2520	Power and cooling on
5b	July 28	31	4380	
6a	July 29	48	2880	Water cooling off
6b	July 31	24	4320	Power and cooling off
6c	August 1	23	5700	Oxygen flow off, mercury thermometer installed
Cal 1W1	August 4	40	2400	Cooling and power on
Cal 1W2a	August 6	29	1740	Power on, cooling off
Cal 1W2b	August 7	41	4200	Power and cooling off

Table 3b - Test results for Experiments #5 and #6

Experiment #	5a		5b		6a		6b		6c	
Date	7/26	7/28	7/28	7/29	7/29	7/31	7/31	8/1	8/1	8/2
Time	1405	0805	0805	1447	1605	1603	1608	1606	1606	1525
Voltage (V)	2.29	2.34	2.34	2.34	2.34	2.34	0	0	0	0
Current (A)	0.706	0.376	0.376	0.329	0.329	0.329	0	0	0	0
Power (W)	1.62	0.88	0.88	0.77	0.77	0.77	0	0	0	0
T_{dewar} (°C)	35.54	36.53	36.53	36.68	36.78	37.29	37.29	36.86	36.86	36.92
ΔT_{dewar} (°C)		0.99		0.15		0.51		-0.43		0.06
$T_{ambient}$ (°C)	35.76	35.77	35.77	35.78	35.37	35.12	35.13	35.27	35.27	35.17
$T_{controller}$ (°C)	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0
$T_{mercury}$ (°C)								36.9	36.9	36.9
$E_{e,in}$ (W·h)	0.14	50.56	0	23.69	0.06	37.06	0	0	0	0
E_{cool} (W·h)	0.13	54.28	0	23.34	0	0	0	0	0	0
$E_{cool}-E_{e,in}$ (W·h)		3.73		-0.35		-37.0		0		0

Table 3b - Test results for Calibrations #1 and #2

Experiment #	Cal 1W1		Cal 1W2a		Cal 1W2b	
Date	8/4	8/6	8/6	8/7	8/7	8/9
Time	1601	0800	0903	1403	1459	0759
Voltage (V)	0.996	0.996	0.998	0.991	0	0
Current (A)	0.988	0.988	0.988	0.988	0	0
Power (W)	0.98	0.98	0.99	0.98	0	0
T_{dewar} (°C)	35.07	35.46	35.65	37.09	37.08	36.84
ΔT_{dewar} (°C)		0.39		1.44		-0.24
$T_{ambient}$ (°C)	35.23	35.20	35.18	34.87	34.88	35.01
$T_{controller}$ (°C)	36.0	36.0	36.0	36.0	36.0	36.0
$T_{mercury}$ (°C)	36.9	36.9	36.9	36.7	36.7	36.9
$E_{e,in}$ (W·h)	0.1	39.44	0.08	29.39	0	0
E_{cool} (W·h)	0.1	40.88	0	0	0	0
$E_{cool}-E_{e,in}$ (W·h)		1.44		-29.4		0

During experiment #5a the cell resistance was increasing, so that the input current decreased from 0.71 A to 0.38 A (power went from 1.62 W to 0.88 W). The power was constant through most of experiment #5b and all through experiment #6a. At the beginning of experiment #6c a mercury thermometer was placed in the enclosure on top of the dewar in order to check the enclosure ambient temperature. From this time until the end of the calibrations the temperature indicated by this thermometer was 36.8±0.1°C.

Following the method used for experiments #1 to #3, the results for experiments #4 to #6 are given in Table 4.

Table 4 - Data from Experiments #4, #5 and #6

Expt. #	Electrical Energy In $E_{e,in}$ (W·h)	Thermal Energy Out E_{cool} (W·h)	Electrolysis Energy E_{elec} (W·h)	Measured Gas Released (L)	Theoretical Gas Production (L)	Calculated Recombination Energy E_{rec} (W·h)
4	142.7	65.4	87.1	21.8	36.8	35.3
5	74.0	77.4	47.2	-	-	47.2
6	36.7	0	23.2	-	-	23.2

(Note that in experiment #6 no heat was possible because the heat exchanger had been turned off. The cell temperature increased 0.51°C)

After studying the results of the last two experiments and the calibration runs, two new terms in the overall energy balance were introduced. The first term (E_{loss}) allowed for the energy that would leak through the dewar walls and lid due to the small difference between the temperature inside and outside the dewar. The second term (E_{cap}) was to account for the storage of heat in the dewar contents (heat transfer fluid and the complete cell), given the difference in temperature in the dewar between the start and end of a run. The terms can be defined:

$$P_{loss} = U(T_{dewar} - T_{ambient})$$

$$E_{cap} = C_{p,dewar}(T_{end} - T_{start})$$

where:

U = overall heat transfer coefficient of the dewar $(W \cdot K^{-1})$

$C_{p,dewar}$ = specific heat of the dewar contents $(W \cdot h \cdot K^{-1})$

The total energy output is thus given by:

$$E_{tot,out} = E_{cool} + E_{elec} + E_{loss} + E_{cap}$$

The value of $C_{p,dewar}$ was estimated to be at least $17.4 \ W \cdot h \cdot K^{-1}$, based on the fact that the dewar had a volume of about 15 L, which, if filled only with water, would give this heat capacity. Given the different materials in the cell and the inner walls of the dewar, a best estimate of the heat capacity of the dewar contents was put at about $20 \ W \cdot h \cdot K^{-1}$. The heat transfer coefficient was estimated from literature data for typical vacuum insulated containers to be between 0.05 and $0.1 \ W \cdot K^{-1}$, although this was expected to be on the low side, because the lid was not tightly sealed.

A number of calibration runs were done to try to determine the values of these two parameters. A number of cooling curves were obtained and from these, coupled with all the other evidence, it was clear that the estimate of the dewar heat capacity was reasonable. However, the heat transfer coefficient was obviously incorrect.

During the calibrations, a check was made of the precision and accuracy of the thermocouples. These were found to be very good, giving temperatures within about $\pm 0.1 \ K$. However, the ambient temperature was determined at the board used for the thermocouple junctions, and during the calibrations this was found to be low by anything up to 2 K. The temperature reading of the enclosure controller was found to be approximately 0.8 K below the actual ambient temperature measured by a calibrated mercury-in-glass thermometer placed close to the lid of the dewar, and this value did not vary by more than 0.2 K over the course of the calibration runs (about five days).

A preliminary analysis of the results for experiment #5a was made with the aid of the results of calibration Cal 1W1, since the two runs had approximately the same duration. During this calibration run, the dewar temperature rose by 0.39 K. Given that there was no electrolysis and the output energy must be equal to the input energy, an energy balance for this situation is thus:

$$\begin{aligned} E_{loss} &= E_{e,in} - E_{cool} - E_{cap} \\ &= 39.44 - 40.88 - 20 \times 0.39 \ W \cdot h \\ &= -9.24 \ W \cdot h \end{aligned}$$

Given that in experiment #5a the measured dewar temperature was always above the dewar temperature in calibration Cal 1W1, the value -9.24 W·h represents a conservative estimate of the energy loss for experiment #5a as long as the ambient temperature was the same for both runs. In this case the energy balance can be calculated:

$$\begin{aligned} E_{tot,out} &= E_{cool} + E_{elec} + E_{loss} + E_{cap} \\ &= 54.15 + 0.0 - 9.24 + 20 \times 0.99 \ W \cdot h \end{aligned}$$

$$\begin{aligned} E_{tot,in} &= E_{e,in} + E_{rec} \\ &= 50.56 + 0.0 \ W \cdot h \end{aligned}$$

$$\begin{aligned} E_{ex} &= E_{tot,out} - E_{tot,in} \\ &= 54.15 - 9.24 + 20 \times 0.99 - 50.56 \ W \cdot h \\ &= 14.15 \ W \cdot h \end{aligned}$$

This excess heat of about 14 W·h is equivalent to 28% of the input energy.

Mathematical Modeling

The above method of analysis includes the assumptions that the ambient temperature and the heat transfer coefficient remained the same through the series of experiments and calibrations. Useful information may be gained by studying the temperature of the system as the power input and cooling were changed. A more powerful means of analyzing the data was to model the system using all the major energy terms (neglecting frictional energy, stirring energy, evaporative enthalpy and lead-wire resistance) as a function of time. The model thus estimated the temperature of the dewar contents as a function of time with the fitted parameters U, $C_{p,dewar}$, T_{start} and $\Delta T_{a,e}$. or $T_{a,e}$. The fitting was done using a least-squares method comparing the measured dewar temperature with the calculated dewar temperature. The following assumptions were made:

- U is independent of temperature
- $C_{p,dewar}$, is 20 W·h·K^{-1}, and

either:
- The ambient temperature recorded at the junction board ($T_{ambient}$) was in error by the constant amount $\Delta T_{a,e}$. The effective ambient temperature ($T_{a,e}$) is thus $T_{ambient} + \Delta T_{a,e}$,

or:
- The ambient temperature was constant and equal to $T_{a,e}$.

The two models represent some conjectures as to what was most strongly influencing the heat loss from the dewar. The constant ambient temperature model goes on the assumption that the enclosure temperature controller was doing its job. The constant error in ambient temperature model assumes that the ambient temperature measurement was still following the enclosure temperature, but was being influenced by some heat source such as the nearby enclosure wall or radiant heat from the enclosure heaters.

Put in its differential form, the model is:

$$T_{dewar,2} = T_{dewar,1} + \frac{\int_{t_1}^{t_2} P_{e,m}\, dt + \int_{t_1}^{t_2} P_{rec}\, dt + \int_{t_1}^{t_2} -P_{cool}\, dt + \int_{t_1}^{t_2} -P_{elec}\, dt + \int_{t_1}^{t_2} -U(T_{dewar} - T_{a,e})\, dt}{C_{p,dewar}}$$

Since the model was integrated numerically, it was first converted to the following difference form:

$$T_{dewar,t+\Delta t} = T_{dewar,t} + \frac{P_{e,in}\Delta t + P_{rec}\Delta t - P_{cool}\Delta t - P_{elec}\Delta t - U(T_{dewar} - T_{a,e})\Delta t}{C_{p,dewar}}$$

and the integration was done using rectangular integration, because the time intervals were so short relative to the rate of change of the measured variables.

The advantage of this model becomes clear after looking at the form of the last equation and noting that the only term that depends on temperature is the heat transfer term (E_{loss}). The significance of this is that the heat transfer term is the only one which will produce a curve in the dewar temperature/time function. Thus, in all the runs (both experiments and calibrations) where there is significant curvature in the dewar temperature, the heat transfer coefficient U can be estimated from the shape of the curve independently of other effects. This, of course, presumes that the excess heat predicted by Mills is not a significant function of temperature (over, at most, 3 K). Note also, however, that the actual estimate of U is somewhat influenced by the estimate of the ambient temperature.

The model can be judged first on how well the modeled dewar temperature matched the measured dewar temperature over the course of a run, and then (most importantly) on whether the parameters

were consistent from run to run and consistent with the estimates. Table 5 summarizes the results of the modeling of the calibration runs (including an earlier, higher-power run) and reports the fitted values of heat transfer coefficient and effective ambient temperature or error in ambient temperature. The term called Standard Error is the square root of the sum of the squares of the differences between the modeled dewar temperature and the measured dewar temperature divided by the number of time intervals in the run. The term E_{net} is defined in the same way as E_{ex} (= $E_{tot,out} - E_{tot,in}$).

Table 5a - Model Fitting Results for Constant Error in Ambient Temperature

Run	Time (h)	Energy in (W·h)	$\Delta T_{a,e}$ (K)	U (W·K⁻¹)	E_{loss} (W·h)	Standard Error (K)	E_{net} (W·h)
Cal 1W1	40.4	39.8	0.28	1.60	-9.35	0.060	-0.43
Cal 1W2	71.5	28.9	1.80	1.65	4.82	0.071	-1.30
Cal 15W	26.2	382.0	0.55	1.46	7.29	0.068	-1.54

Table 5b - Model Fitting Results for Constant Ambient Temperature

Run	Time (h)	Energy in (W·h)	$T_{a,e}$ (°C)	U (W·K⁻¹)	E_{loss} (W·h)	Standard Error (K)	E_{net} (W·h)
Cal 1W1	40.4	39.8	35.49	1.82	-9.75	0.060	-0.84
Cal 1W2	71.5	28.9	36.72	1.37	7.73	0.095	1.61
Cal 15W	26.2	382.0	38.08	1.51	-25.92	0.140	-8.78

The figures given in the Appendix (Figures A1 to A6) present the results of the modeling for the calibration runs, showing the match between measured and calculated dewar temperature. From the standard errors in Tables 5a and 5b and from Figures A1 to A6, it is clear that the constant error in ambient temperature model is much more consistent with the experimental results. This model was therefore selected to perform the analysis of the experiments. Another reasonable assumption is that the heat transfer coefficient is constant. While some reservations might be held about the possible variation in U because of the way the top of the dewar may be placed from run to run, with such high values of U as are given in Tables 5a and 5b, it is expected that the dewar must have lost its vacuum and therefore the dewar walls must be the main area of heat loss compared with the 50 mm thick polystyrene top. The best value to assume for U would appear to be 1.46 W·K⁻¹ since this was calculated for the higher power run where errors are expected to be less.

A slightly troubling result of the modeling is the low ambient temperature during calibration run Cal 1W1. If we believe the temperature shown by the mercury thermometer represents the true effective ambient temperature, then $T_{a,e}$ is low by at least 1.2°C. If, conversely, the ambient temperature is fixed at 36.7°C, then the best fit for the heat transfer coefficient is found to be 0.15 W·K⁻¹ and the standard error is 0.075 K. For comparison, Figure A2a shows the result of this set of parameters. Clearly, the fit is poor and the value of the heat transfer coefficient is too low to be credible.

In order to look at the experiments, two approaches could be taken. The first is to repeat the modeling following the method used for the calibration runs and look at the parameters which are fitted to see if they are reasonable. The second approach might be to modify the model slightly to allow for another parameter, namely E_{ex} with the simple assumption that P_{ex} would be constant over an experiment The modification would be simply:

$$T_{dewar,2} = T_{dewar,1} + \frac{\int_{t_1}^{t_2} P_{e,in}\, dt + \int_{t_1}^{t_2} P_{rec}\, dt + \int_{t_1}^{t_2} -P_{cool}\, dt + \int_{t_1}^{t_2} -P_{elec}\, dt + \int_{t_1}^{t_2} -U(T_{dewar} - T_{a,e})\, dt + \int_{t_1}^{t_2} P_{ex}\, dt}{C_{p,dewar}}$$

and thus:

$$T_{dewar,t-\Delta t} = T_{dewar,t} + \frac{P_{e,in}\Delta t + P_{rec}\Delta t - P_{cool}\Delta t - P_{elec}\Delta t - U(T_{dewar} - T_{a,e})\Delta t + P_{ex}\Delta t}{C_{p,dewar}}$$

Using the first approach, we can assume that the ambient temperature error is constant over the entire experiment, i.e. it is not necessary to divide the experiments into #5a and #5b, or #6a, #6b and #6c. Table 6a presents the results of this model.

Table 6a - Model without P_{ex}

Run	Time (h)	Energy in (W·h)	$\Delta T_{a,e}$ (K)	U (W·K⁻¹)	E_{loss} (W·h)	Standard Error (K)	E_{net} (W·h)
Expt #4	93.6	142.7	1.21	1.46	0.9	0.086	0.2
Expt #5	73.0	74.0	0.91	1.46	-28.0	0.064	-0.8
Expt #6	93.4	36.7	1.70	1.46	38.7	0.089	3.5

Table 6b gives the results of the model with P_{ex} included.

Table 6b - Models with P_{ex}

Run	Time (h)	Energy in (W·h)	$\Delta T_{a,e}$ (K)	U (W·K⁻¹)	E_{loss} (W·h)	Standard Error (K)	E_{ex} (W·h)	E_{net} (W·h)
Expt #4	93.6	142.7	1.07	1.46	20.0	0.086	19.2	0.2
Expt #5	73.0	74.0	0.82	1.46	-18.1	0.064	9.9	-0.8
Expt #6	93.4	36.7	1.65	1.46	44.8	0.078	6.0	3.5

In this model the excess energy term was found to be between 10% and 15% of the input energy. Figures are included in the Appendix showing the measured and predicted dewar temperature for all the above cases (Figures A7 to A12). There is clearly a better fit for experiment #6 when the excess heat term is included.

Table 7 summarizes the results of the energy balances, showing that E_{net} is within ±5% of the input electrical energy, except for run #6. The difficulty however, lies in deciding whether the model parameters are reasonable and whether there is any way to choose between the two models.

Table 7 - Overall Energy Balance Terms

Run	$-E_{e,in}$ (W·h)	$-E_{rec}$ (W·h)	E_{cool} (W·h)	E_{elec} (W·h)	E_{loss} (W·h)	E_{cap} (W·h)	E_{ex} (W·h)	E_{net} (W·h)
Expt #4	-142.7	-35.3	65.4	87.1	0.9	24.9	-	-0.4
Expt #5	-74.0	-47.2	77.4	47.2	-28.0	23.8	-	-0.7
Expt #6	-36.7	-23.2	0	23.2	38.7	1.4	-	3.2
Expt #4	-142.7	-35.3	65.4	87.1	20.0	24.9	19.2	-0.4
Expt #5	-74.0	-47.2	77.4	47.2	-18.1	23.8	9.9	-0.7
Expt #6	-36.7	-23.2	0	23.2	44.8	1.4	6.0	3.2

4.   DISCUSSION

In the higher power experiments (#1, #2 and #3), no net excess or deficit energy was observed greater than experimental error. According to Mills, this result was consistent with operation at currents and voltages substantially higher than 1 mA·cm^{-2} and 2.5 V. The lower power experiments were done within the recommended current density and voltage, and according to Mills the expected excess heat would be about 0.25 W. Various methods of analysis were applied to the results of experiments #4, #5 and #6. Some of these analyses indicated possible excess heat at approximately this level.

In experiments #4, #5 and #6, an effort was made to model the results in a consistent manner to account for the observations. The parameters that were used in the models were chosen because they were either unknown or appeared to be measured incorrectly. However, they were not expected to vary widely or completely randomly. In all models the ambient temperature correction was not very consistent. This variation may well be related to the total heat load on the system enclosure temperature control system. The effective ambient temperature was not consistent either (and the corresponding model was consequently not used to analyze the experiments), even though the temperature controller for the enclosure was absolutely steady (apparently), as was the thermometer that was placed in the enclosure during experiment #6c (at least within 0.2 K).

It seemed reasonable to assume a constant value of U from the results of the higher power calibration and use this for all analyses. However, this would only be valid if the heat transfer is just through the dewar walls. If significant heat transfer occurs through the lid, the value of U would change each time the lid was removed and replaced.

It is instructive and revealing to consider the sensitivity of the results to the different parameters used in the modeling. The most critical is the ambient temperature estimate. If we take an average heat transfer coefficient of say 1.5 W·K^{-1} and an average experiment duration of 60 hours, then a 0.1 K error in the ambient temperature corresponds to an error of 9 W·h in the heat loss term, which is approximately equal to the magnitude of the expected excess heat. It is unlikely that any of our temperature measurement were within this level of accuracy and it was unfortunate that the dewar had such poor insulating properties.

In fact the above calculation for the sensitivity of the heat loss to the ambient temperature also applies to the temperature inside the dewar. It is very likely that in the unstirred dewar, there would have been significant temperature gradients, especially top-to-bottom. It would be reasonable to assume that such temperature gradients in the dewar during calibration runs would be quite different from the gradients during closed cell operation with the recombiner. More than half the heat in experiments #5 and #6 was released to the dewar contents in the top of the cell where the recombiner was placed. In other cases, calibrations or open cell operation, all or most of the heat is released through the electrolyte in the lower part of the cell. There is no obvious way to deduce the magnitude of the temperature gradients from the results presented here.

Both the temperature inside the dewar and the ambient temperature were point measurements. Total heat loss from the dewar depends on the heat lost from all parts of the dewar surface and therefore is affected by the any temperature profiles either inside or outside. Point measurements can, at best, only be an indication of the average temperature. The modeling is an attempt, with only limited success, at finding an *effective* ambient temperature which is consistent with the measured temperature-time function in the dewar. Stirring the dewar contents, circulating the ambient air and using non-radiant heat in the enclosure would have significantly improved the representativeness of the point temperature measurements.

In experiment #4 an open cell was used and the off gases vented through a mass-flow transducer. With the low-voltage experiments the off-gases were typically evolved at a rate of 3 mL·min^{-1} (compared to a flow rate of 26 mL·min^{-1} in the higher voltage experiments). At low flow rates, the absolute accuracy of the mass-flow transducer used was a source of some concern, but from the data we have there would appear to be a higher recombination rate in experiment #4 than in experiments #1 and #2. This fits with the expected mechanism for recombination, which is the reaction between each of the gases with nascent gas bubbles at the opposite electrode — especially at the anode, which was made of the highly catalytically active material, platinum. Recombination is strongly promoted by stirring the electrolyte, as was done in these experiments. If, however, it is assumed that none of

the electrolysis gases recombine, the energy balance for this experiment (see Table 7) seems to indicate that up to 54.5 W·h of excess heat was produced (35.3 W·h + 19.2 W·h). This figure corresponds to 38% of the electrical input energy and agrees with the amount predicted by Mills.

A major part of this work was the development of a model to simulate the heat transfer characteristics of the calorimeter. The model, which includes the thermal capacity of the dewar contents and the heat exchange through the dewar walls and top, was reasonably successful in closing the energy balance except for experiment #6. Assuming a constant ambient temperature of 36.70°C, the results of experiment #6 would indicate about 14 Wh of excess heat produced. This figure corresponds to 38% of the electrical input energy. This result agrees with the amount predicted by Mills.

Experiments #4, #5 and #6 stretched the capabilities of the experimental system to the limit. Any further work in this area would require more sensitive and accurate temperature-measuring devices, and a considerably more efficient dewar.

5.   REFERENCES

1.   P.L. Hagelstein, Summary of the Third International Conference on Cold Fusion, Presented at MIT, 1993 January 16.

2.   E. Storms, Fusion Technology, 20, 433 (1991).

3.   R.T. Bush, Fusion Technology, 22, 301 (1992).

4.   R. Notoya and M. Enyo, Proc. ICCF3, Dec (1992).

5.   R. Mills and S.P. Kneizys, Fusion Technology, 20, 65 (1991).

6.   R. L. Mills, W.R. Good and J.J. Farrell in *Unification of Spacetime, the Forces, Matter and Energy*, 1992, Science Press, Pa.

7.   W.A. Good, Personal Communication 1993, June 8.

8.   JANAF Thermochemical Tables, Third Edition, 14, (1), 1274 (1985)

9.   Handbook of Physics and Chemistry, 71 st Edition, CRC Press, 15-30 (1991)

10. R.H. Perry and D.W. Green, *Perry's Chemical Engineers' Handbook*, 6th edition, McGraw-Hill, 1984.
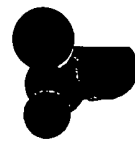
Appendix
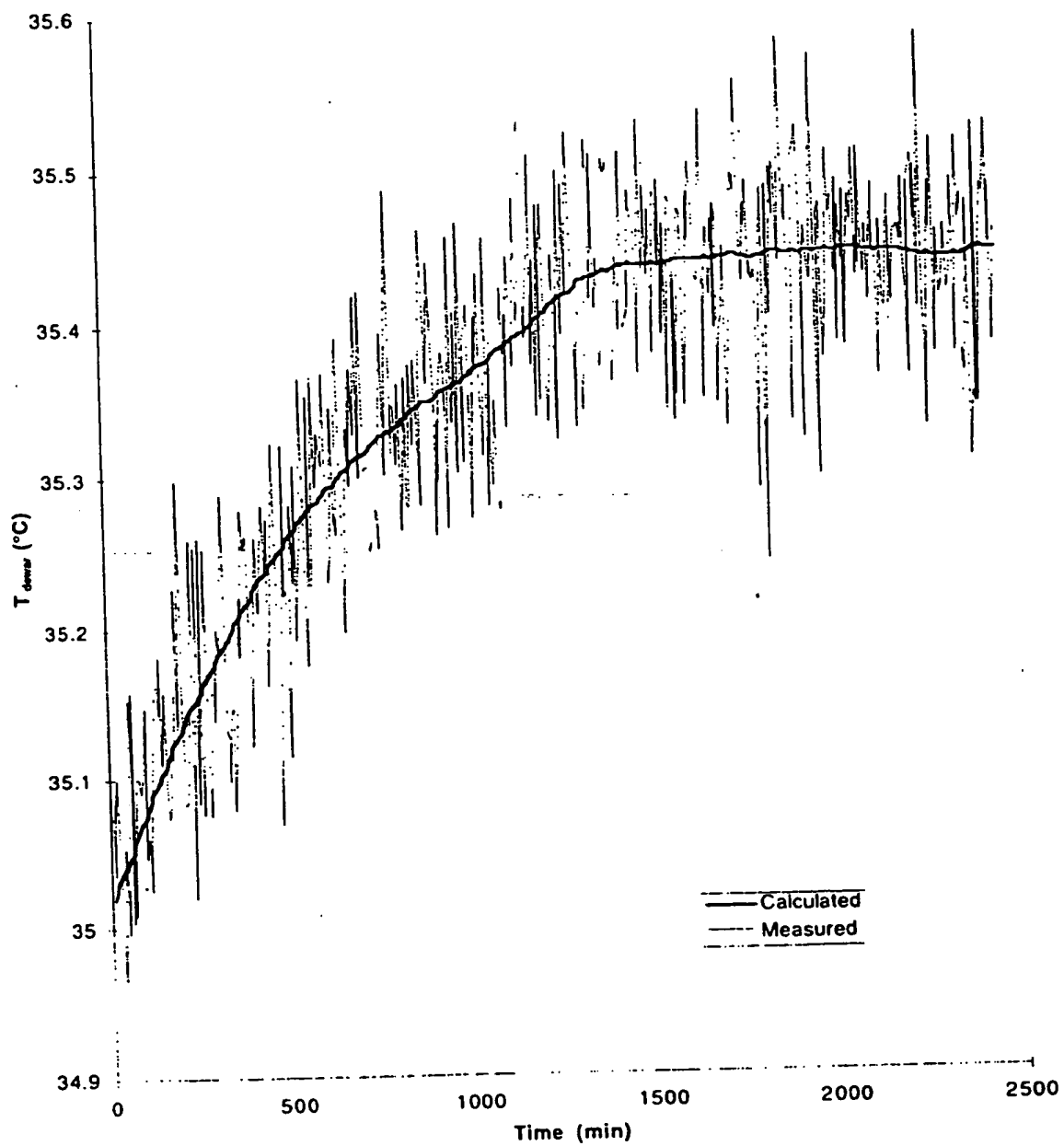
Figure A1 - Dewar Temperature Modelling in Calibration Cal1W1
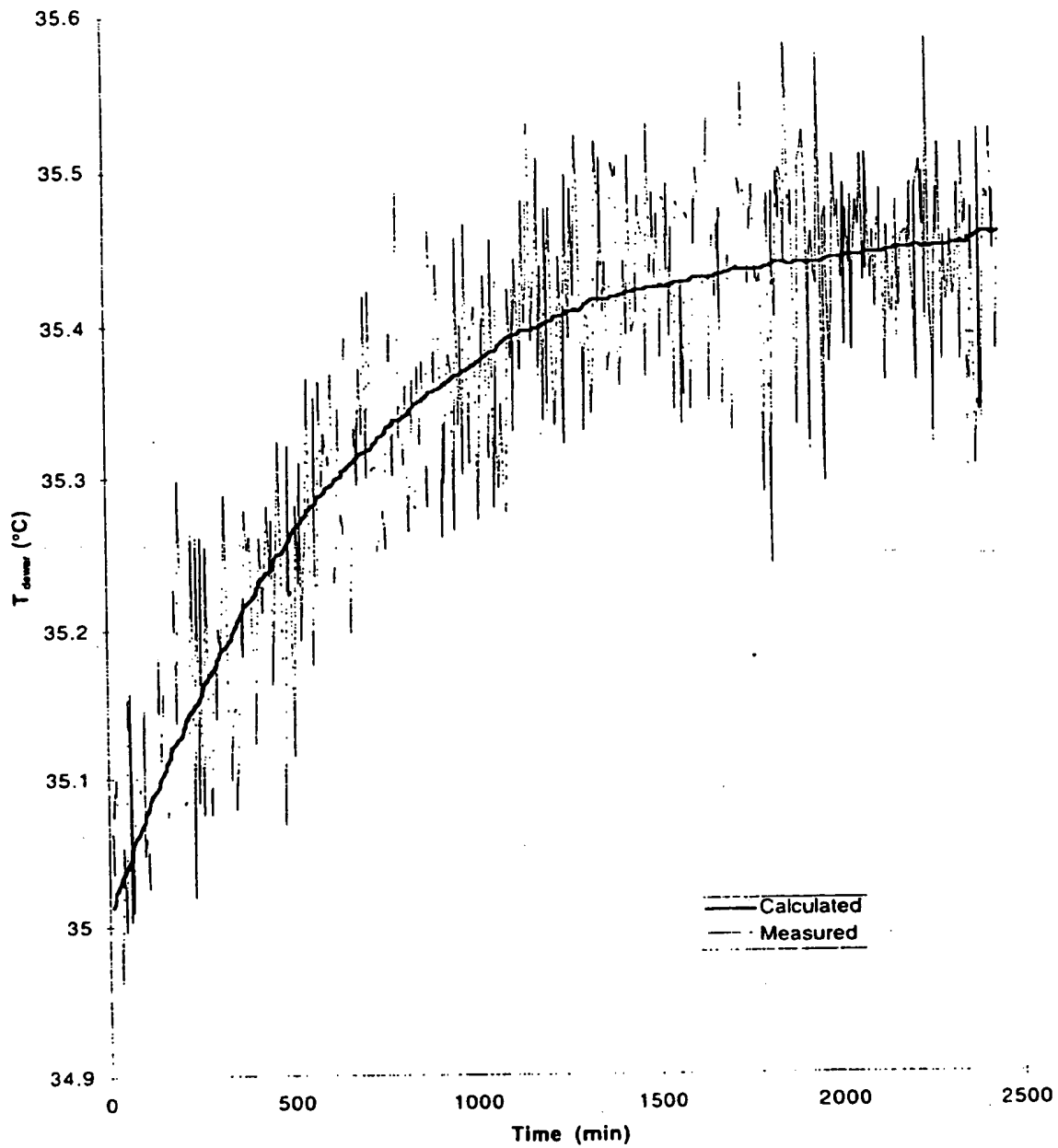using Constant Error in Ambient Temperature

**Figure A2 - Dewar Temperature Modelling in Calibration Cal1W1
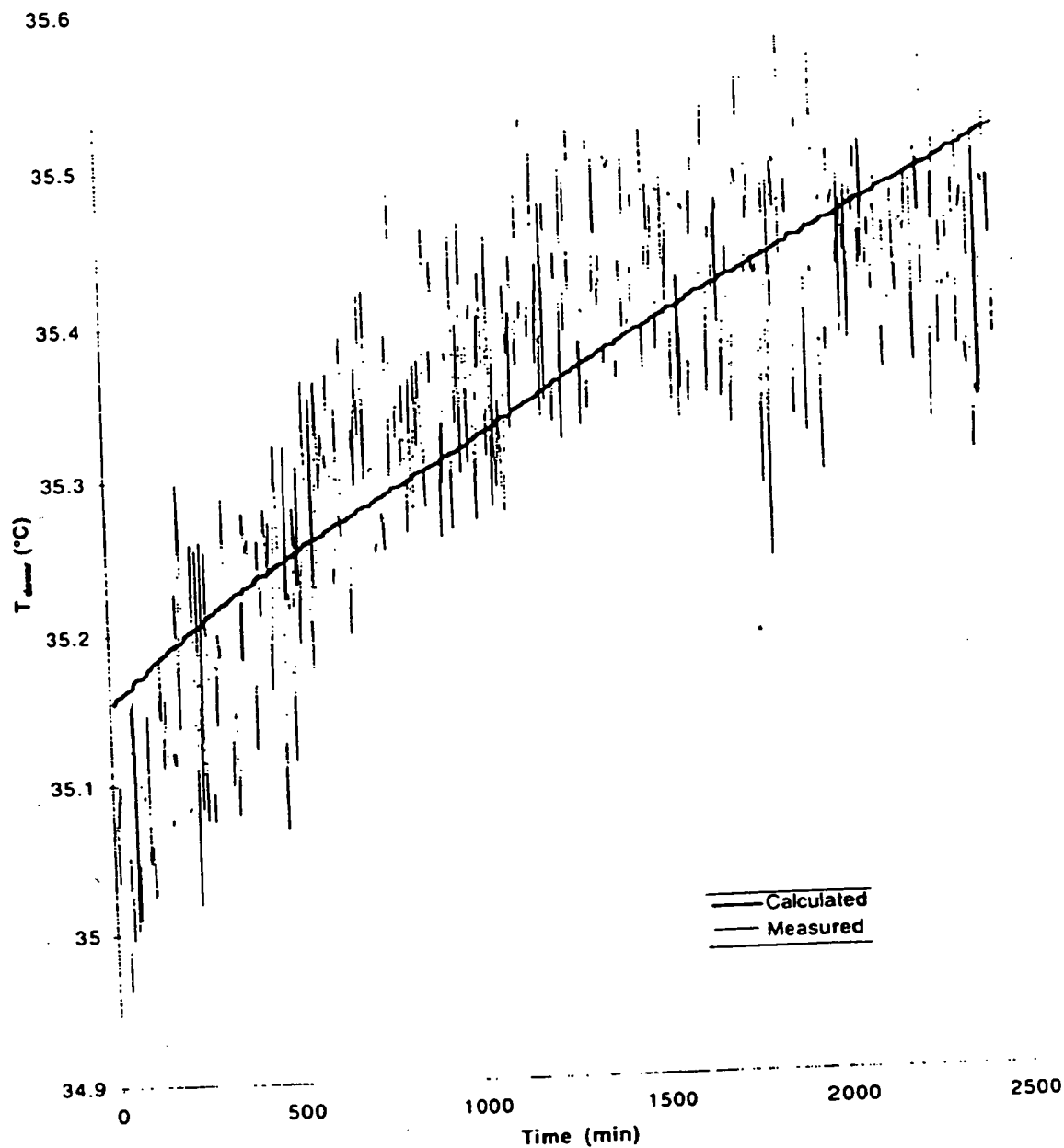using Constant Ambient Temperature**

Figure A2a - Dewar Temperature Modelling in Calibration Cal1W1
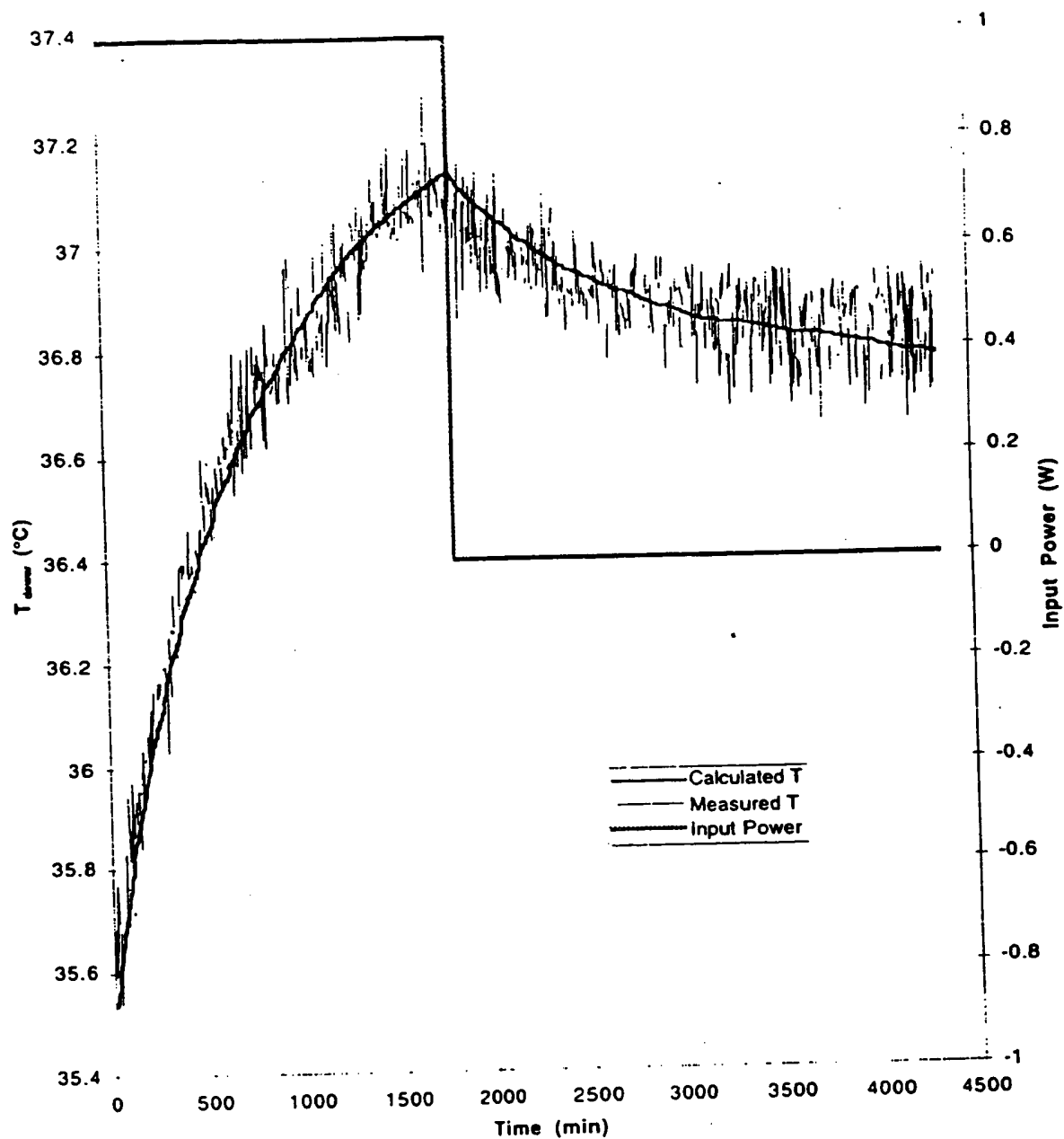using Ambient Temperature set to 36.7°C

Figure A3 - Dewar Temperature Modelling in Calibration Cell W2
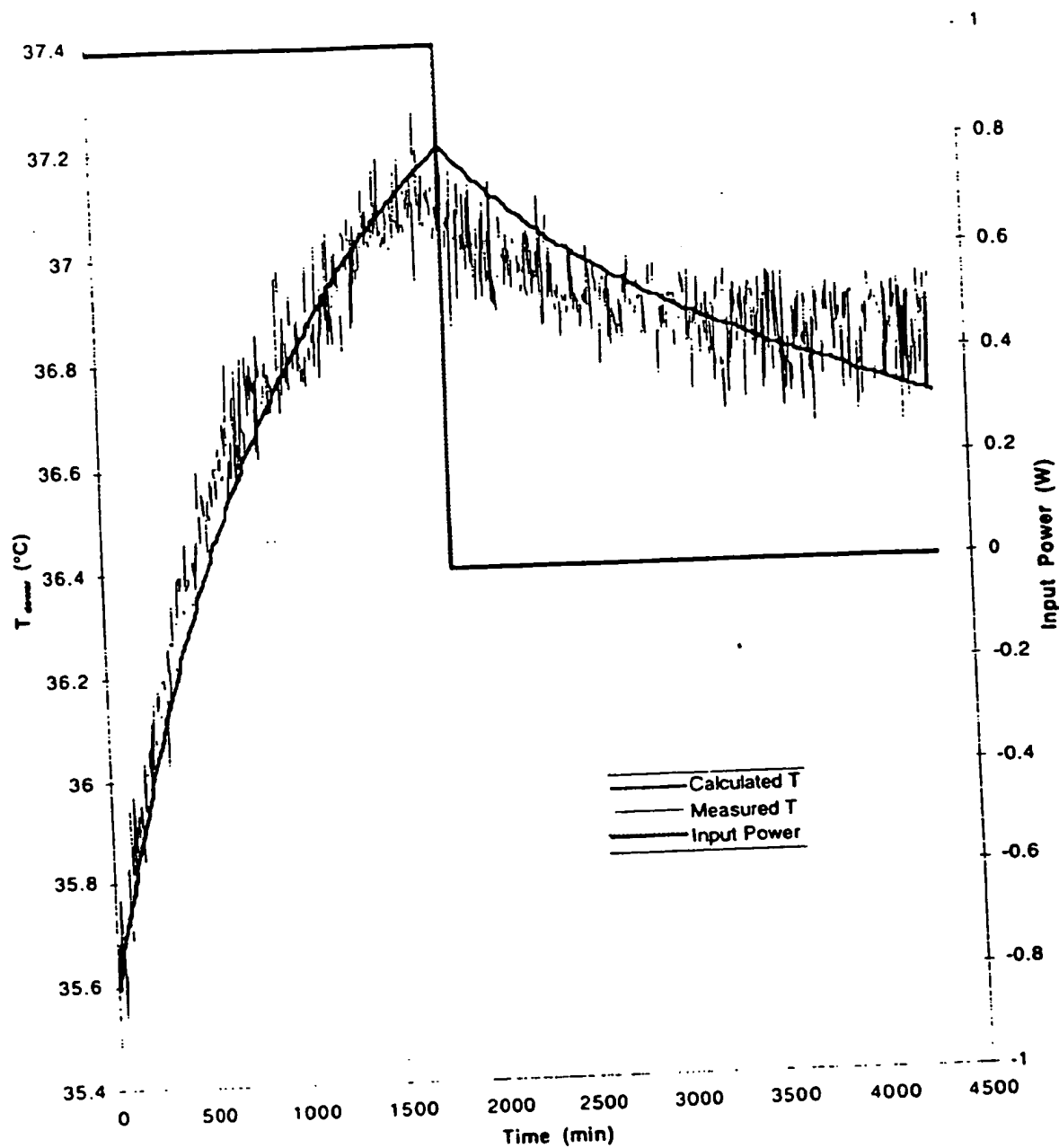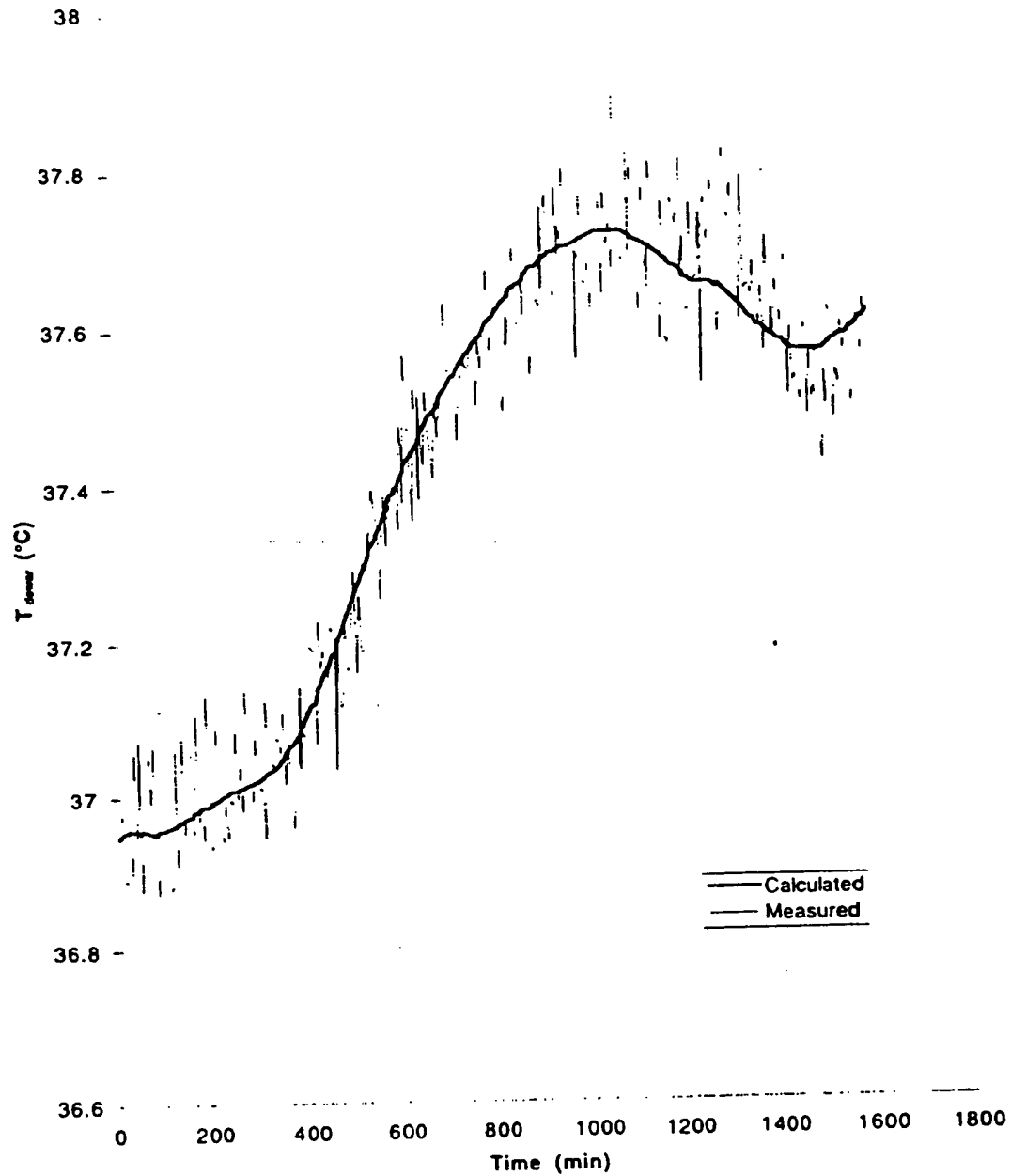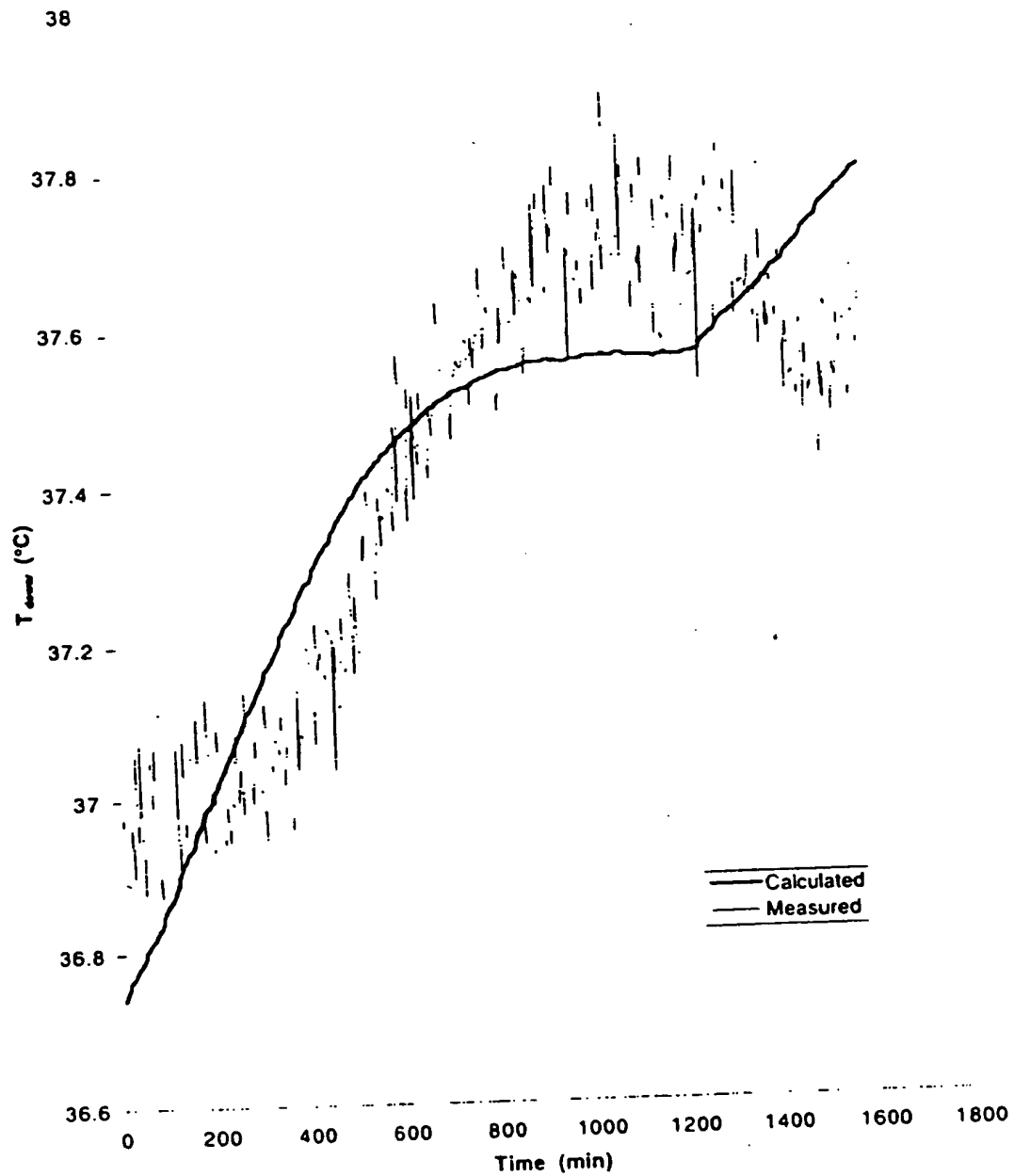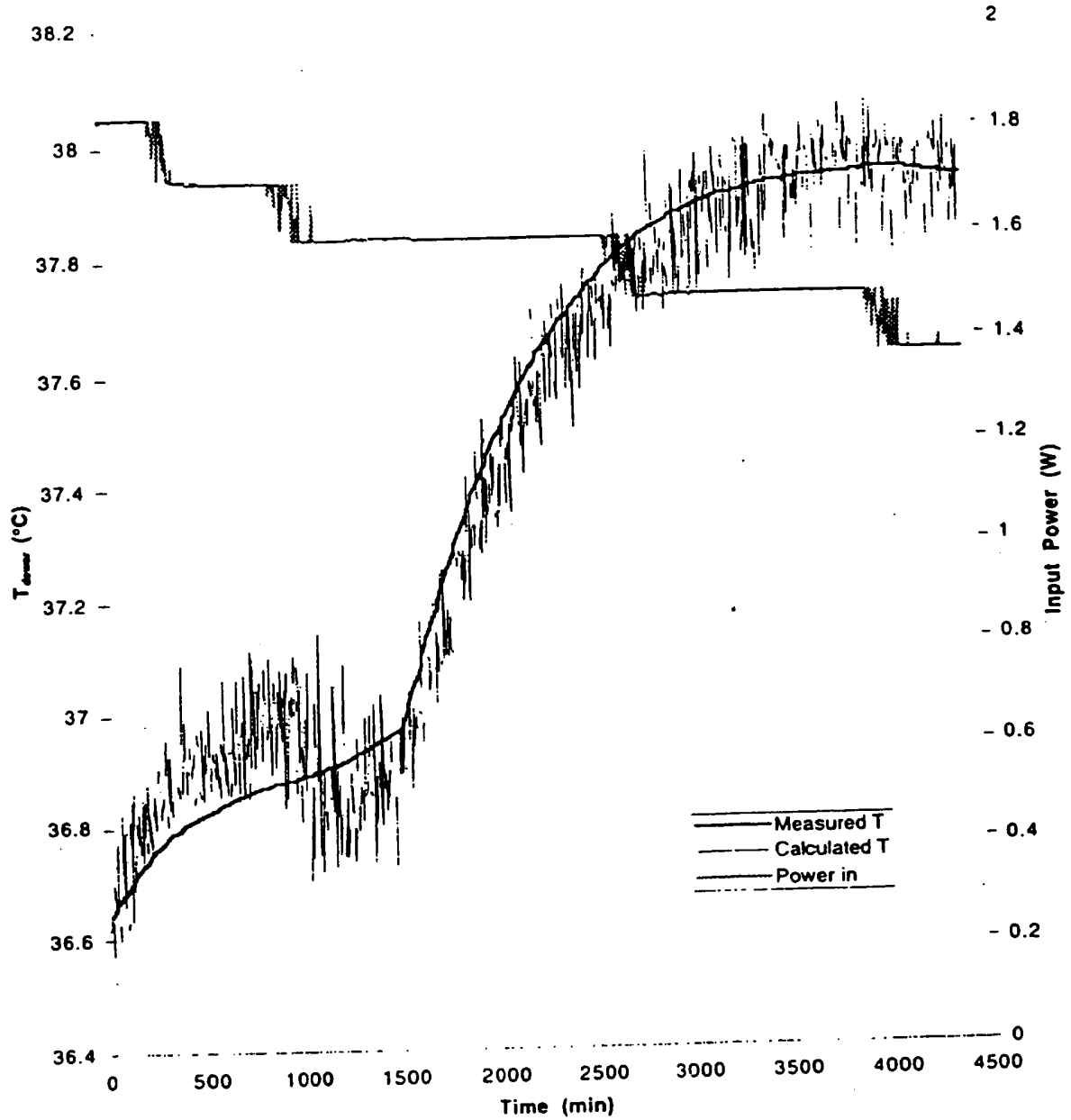using Constant Error in Ambient Temperature

Figure A4 - Dewar Temperature Modelling in Calibration Cal1W2
using Constant Ambient Temperature

Figure A5 - Dewar Temperature Modelling in Calibration Cal15W
using Constant Error in Ambient Temperature

Figure A6 - Dewar Temperature Modelling in Calibration Cal15W
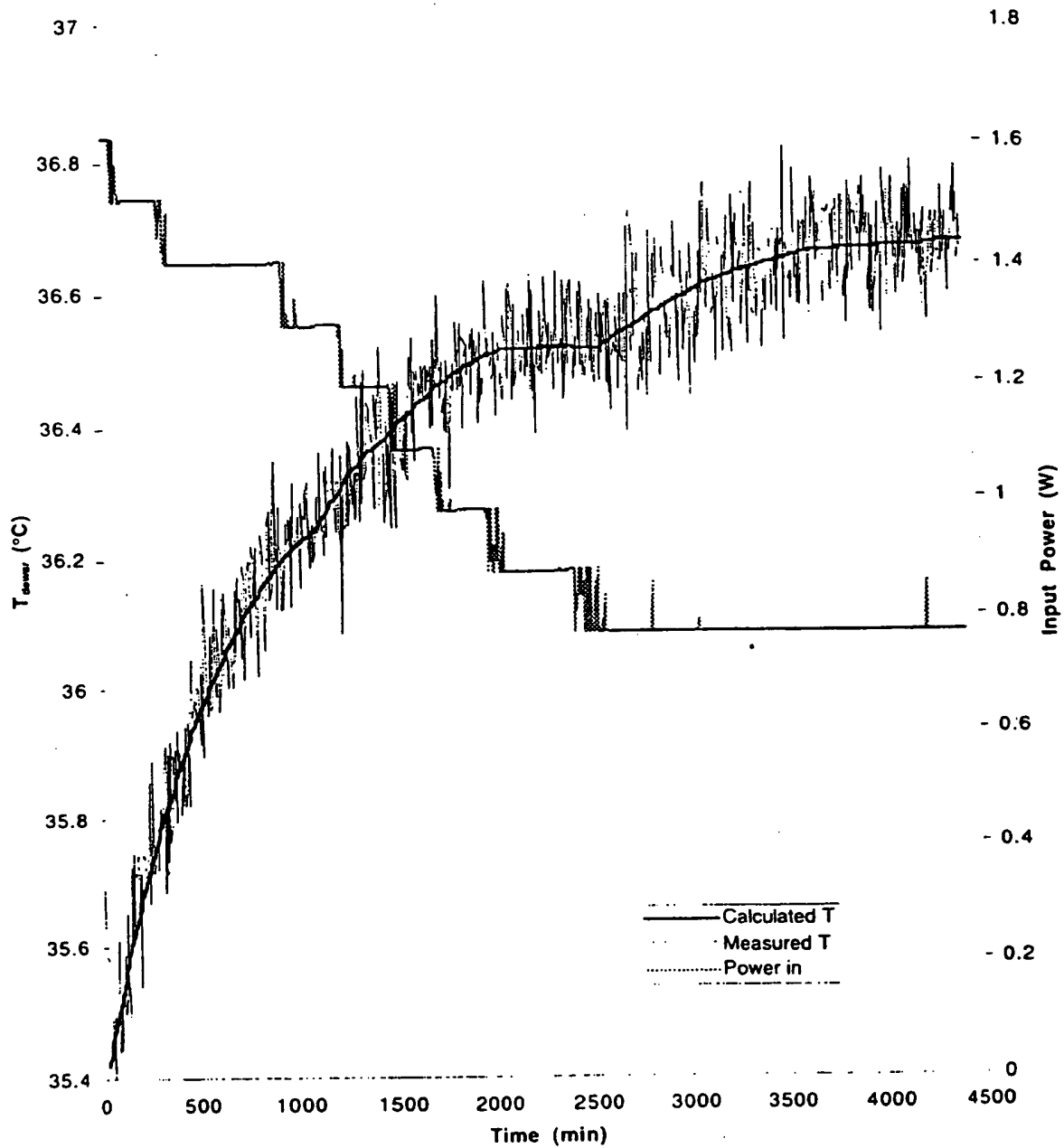using Constant Ambient Temperature

Figure A7 - Dewar Temperature Modelling in Experiment #4
using Constant Error in Ambient Temperature and $P_{ex}=0$
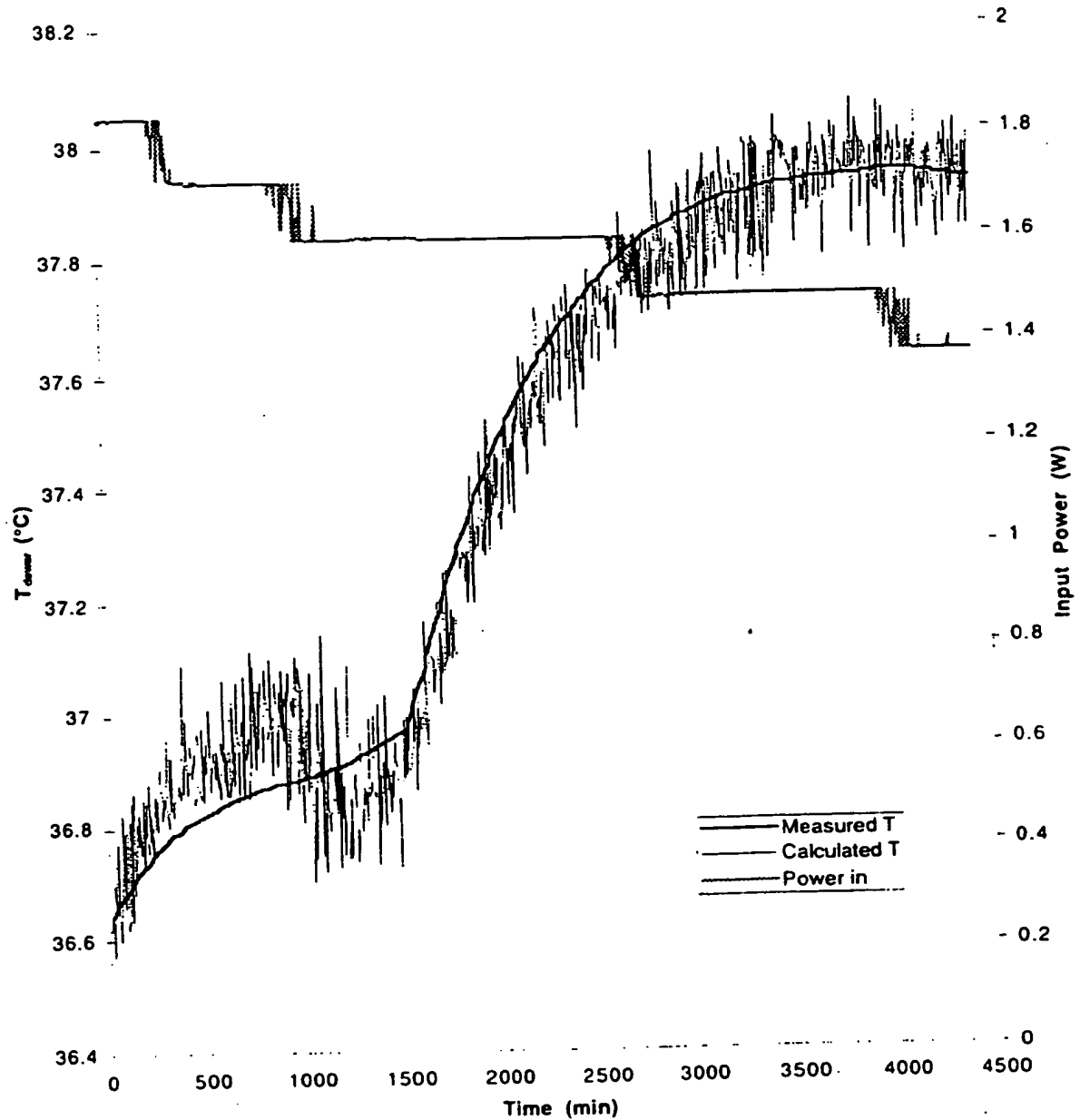
Figure A8 - Dewar Temperature Modelling in Experiment #4
using Constant Error in Ambient Temperature and $P_{ex} \neq 0$

Figure A9 - Dewar Temperature Modelling in Experiment #5
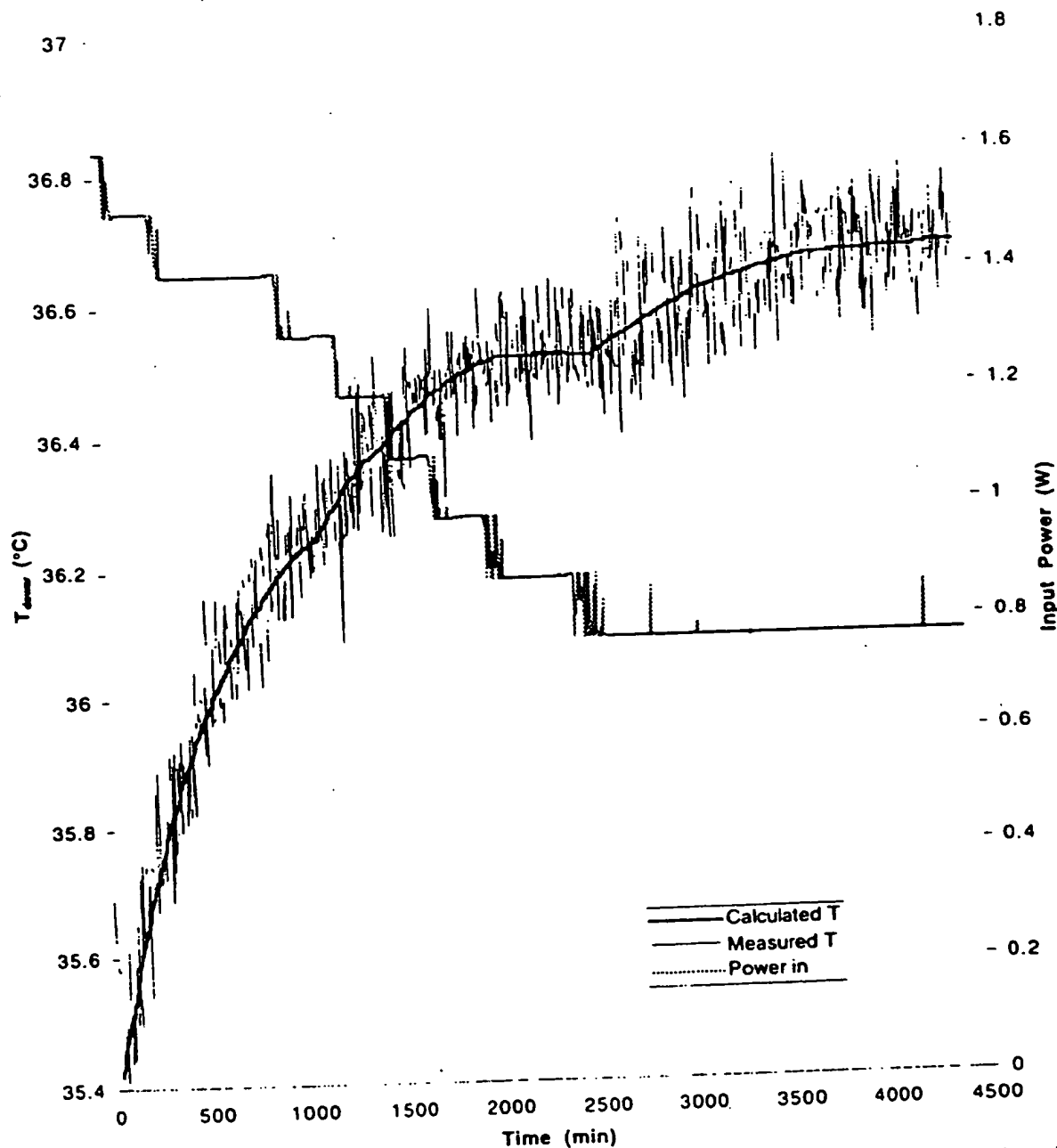using Constant Error in Ambient Temperature and $P_{ex}=0$

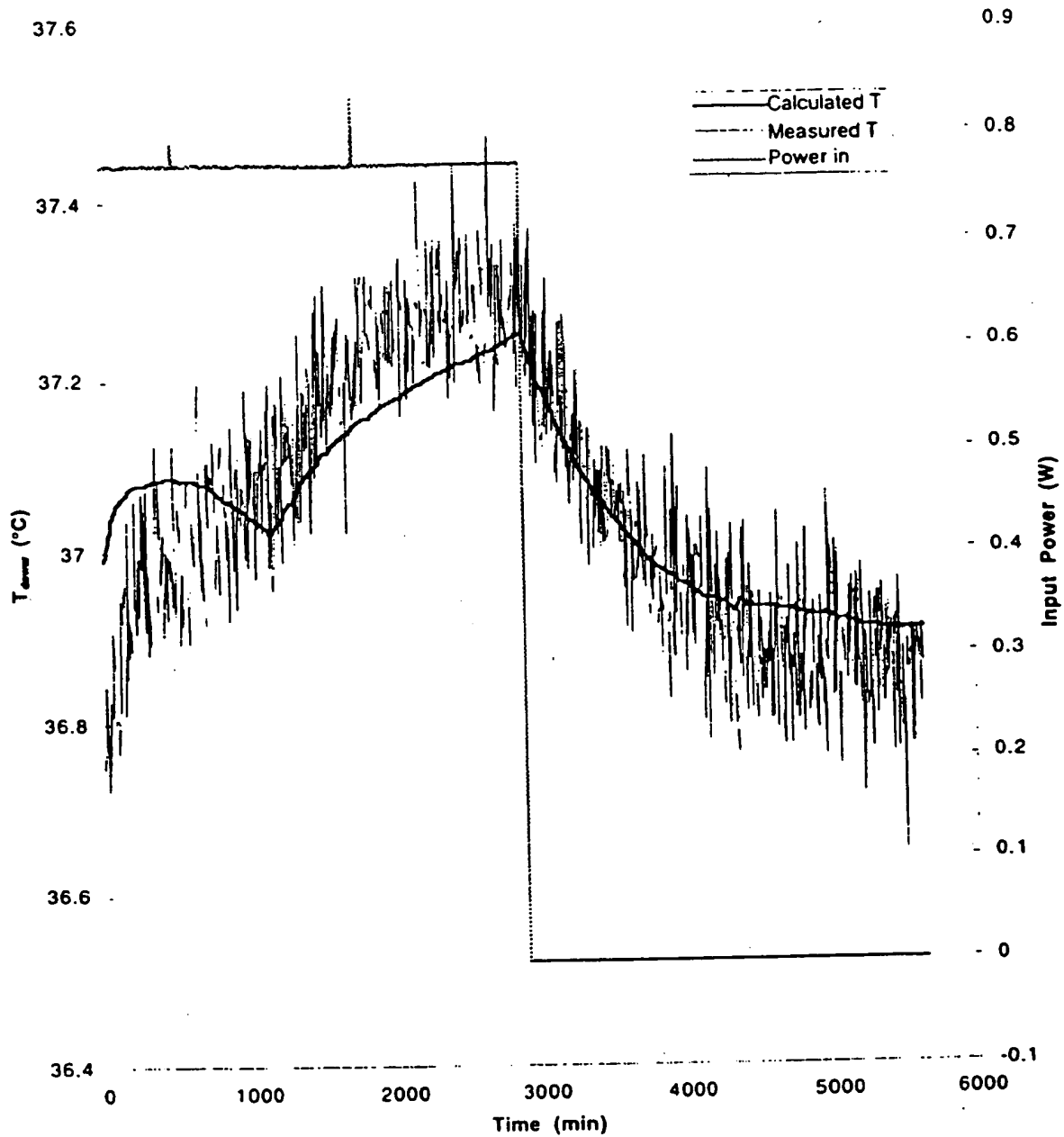Figure A10 - Dewar Temperature Modelling in Experiment #5 using Constant Error in Ambient Temperature and $P_{ex}=0$

Figure A11 - Dewar Temperature Modelling in Experiment #6
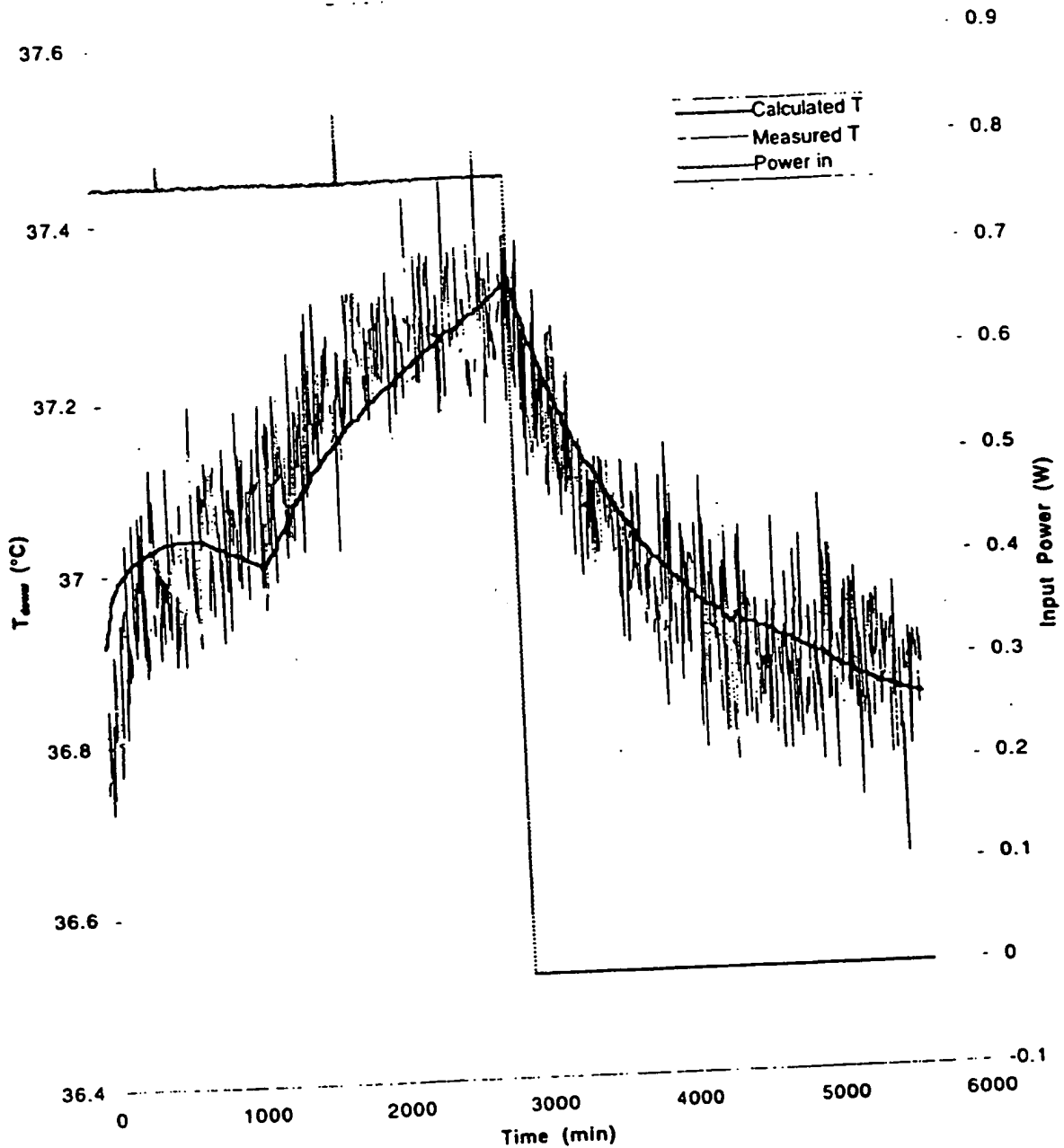using Constant Error in Ambient Temperature and $P_{ex}=0$

Figure A12 - Dewar Temperature Modelling in Experiment #6
using Constant Error in Ambient Temperature and $P_{ex} \neq 0$

THIS PAGE BLANK (USPTO)